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THE KINETICS OF  
R E A C T I O N S  
IN  
S O L U T I O N



THE KINETICS OF  
REACTIONS  
IN  
SOLUTION

BY

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SECOND EDITION

OXFORD  
AT THE CLARENDON PRESS

*Oxford University Press, Amen House, London E.C. 4*

GLASGOW NEW YORK TORONTO MELBOURNE WELLINGTON  
BOMBAY CALCUTTA MADRAS CAPE TOWN

*Geoffrey Cumberlege, Publisher to the University*

*By the same Author*

PHYSICAL CHEMISTRY

*Cambridge University Press, 1940*

*First published 1933  
Second edition 1947*

Reprinted photographically in Great Britain in  
1950 at the OXFORD UNIVERSITY PRESS from  
sheets of the second edition

## PREFACE TO THE SECOND EDITION

THE FIRST EDITION of this book was based on the realization, compelling to me a few years before its appearance, that the collision theory, as applied by Trautz and by Lewis to gas reactions, was equally applicable to a variety of chemical changes in solution. These included ionic reactions, substitutions at the saturated carbon atom, and catalyses, whether polar, ionic, or heterogeneous. Fortunately it is not necessary to deal in detail with the recent growth in these important branches, still less with their off-shoots; specialized monographs on such topics have since appeared in adequate numbers, and I refer to them in the text. I concern myself here with the broad outlines of development up to the outbreak of war (subsequent work has been negligible in this country and unimportant elsewhere), and with directions from which further advances may, in my opinion, be expected. The main line of the original work has also been related to a number of contiguous topics, such as colloid stability, ionic structure, and organic reactivity.

My indebtedness is now much greater than in 1933, and includes the Royal Commission for the Exhibition of 1851, who awarded me a Senior Research Scholarship, and the Council of the Royal Society, who elected me Messel Research Fellow. The Royal Commission and the Royal Society let me seek knowledge where I would. After Oxford, research in Germany, and a tour through Russia, I eventually arrived at Cambridge. It is to be hoped, therefore, that this work is free of the parochialism which unfortunately, and yet so loyally, may taint the treatment of those whose experience is largely limited to one centre of learning.

By discussion and criticism in the various Chemical Departments of this University, I have been corrected, guided, and helped by all my colleagues, and in particular by Professor E. K. Rideal and Professor Sir John Lennard-Jones. In the period under review, Professors Max Bodenstein and Thomas Martin Lowry have died, and, although I am exceptionally fortunate in enjoying as close a fraternity with Professor K. F. Bonhoeffer and Professor R. G. W. Norrish, their distinguished successors in the chairs of Physical Chemistry at Berlin and Cambridge, my sense of loss remains. These two pioneers, whose classical researches in chemical kinetics date from the end of

## PREFACE

the last century, looked with tolerance and sympathy on my own work, and enlisted my co-operation in collaborate efforts which their death has brought to an end.

The task of proof-reading has been willingly shared by those who at present share also my researches—Mr. R. Hurst, of New Zealand, Mr. D. Pattanayak, of Patna, and Professor H. A. Puente, of Buenos Aires. In checking the references to over a thousand authors, I have had the valuable assistance of Miss Betty Bond, Librarian to the Cambridge Philosophical Society. Finally, I wish to express my thanks to the officers of the Clarendon Press for showing me at all times a courtesy as unrivalled as is the workmanship of their craftsmen.

E. A. M.-H.

*Cambridge, 1947*

## ACKNOWLEDGEMENTS

FOR permission to reproduce diagrams or tables of data, grateful acknowledgement is made to Dr. A. E. Alexander, Mr. R. P. Bell, Prof. C. E. K. Branch, Prof. J. N. Bronsted, Dr. Arthur W. Chapman, Prof. J. Faringdon Daniels, Dr. J. F. J. Dippy, Dr. D. P. Evans, Dr. J. J. Gordon, Prof. Han s von Halban, Dr. Brynmor Jones, Dr. Martin Kilpatrick, Dr. Arthur B. Lamb, Prof. V. K. La Mer, Prof. R. Livingston, Dr. W. M. Magdin, Dr. Christina C. Miller, Dr. V. G. Morgan, Prof. D. M. Newitt, Prof. A. C. Nixon, Prof. J. N. Northrop, Dr. K. Pitzer, Prof. M. Polanyi, Prof. E. K. Rideal, Dr. F. W. Soper, Dr. R. C. Traill, Dr. A. Wassermann, and Dr. H. B. Watson.

*From the*  
**PREFACE TO THE FIRST EDITION**

I HAVE written this book to show that reactions in solution, that is to say, the phenomena of chemical change in general, can profitably be examined in the light of the kinetic theory—an hypothesis which seven years ago was focused upon, but believed to be restricted to, the comparatively few reactions which occur in gases. It will be observed that the theory brings coherence to a large number of diversified phenomena, and can therefore be said to have stood the pragmatic test.

In a book of this scope, reference can be made to but a relatively small number of chemical reactions. The examples selected are, however, sufficiently representative to portray a miniature, but not too distorted a picture of the whole field of inquiry. I have purposely applied the kinetic theory in a simple manner, partly on account of the inherent difficulties which the problem obviously presents, and partly because the task is primarily to decide whether the principle underlying its application is valid. It may prove to be otherwise: I have made every effort to indicate clearly what are the theoretical explorations, and what the actual facts.

*Oxford, 1933*

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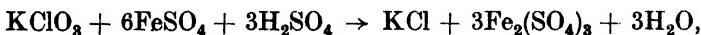
# I

## THE COLLISION THEORY

CANE sugar dissolved in water may be kept almost indefinitely at room temperatures. In the presence of decinormal acid, however, the sugar is converted at a measurable velocity into glucose and fructose, and the chemical change is virtually complete at the end of one day. These well-known facts raise two questions. Why does the reaction not take place in the absence of acid? Why does the reaction in its presence end in a day rather than in a second or a century? The science of chemical kinetics sets out to answer these and similar questions by a formal treatment of all the factors which may determine or influence the velocity of chemical change. In the development of the subject the inversion of cane sugar occupies a prominent position as the first chemical change to be timed<sup>†</sup> and one of the first reactions in the study of which the importance of temperature was realized.<sup>‡</sup> This reaction has attracted the attention of hundreds of investigators, and over one thousand publications dealing with its kinetics have appeared since the days of Wilhelmy.<sup>§</sup> That we are still very far from understanding its mechanism is an illuminating comment on the difficulties attending the problem in general. It is, however, precisely owing to such difficulties that there is no abatement of interest in the kinetics of reactions in solution.

### *The Equation of Arrhenius*

The rate at which chemical change proceeds in any system is denoted by its velocity coefficient,  $k$ , which is simply the number of molecules reacting per unit time when the concentration of each reactant is unity. Numerous attempts<sup>||</sup> were made in the early days of the subject to find the true relation between the velocity coefficient and the absolute temperature,  $T$ . The first investigator to succeed was Hood,<sup>††</sup> who, in a careful examination of the reaction



<sup>†</sup> Wilhelmy, *Pogg. Annalen*, **81**, 413, (1850).

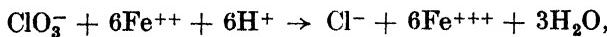
<sup>‡</sup> Arrhenius, *Z. physikal. Chem.*, **4**, 226, (1889).

<sup>§</sup> A list of the first few hundred papers is given by Caldwell, *British Association Reports*, p. 351, (1906).

<sup>||</sup> Summarized by Trautz and Volkmann, *Z. physikal. Chem.*, **64**, 53, (1908).

<sup>††</sup> *Phil. Mag.*, **6**, 371, (1878); *ibid.*, **20**, 323, (1885).

which we would now write as follows



found an exponential relation between the velocity coefficient and the temperature:

$$\ln k = A' - \frac{E_A}{RT}. \quad (1)$$

As guarded in his conclusions as he was thorough in his experiments, he made no attempt to generalize his findings, but held them to be true for 'this reaction at least'.

Hood's equation was by no means universally adopted. The most persistent opposition to it came from Harcourt and Esson,† who claimed, somewhat dogmatically, that the equation

$$k = \text{constant} \times T^m, \quad (2)$$

where  $m$  is positive, was the correct one, and of general applicability. Svante Arrhenius (*loc. cit.*) favoured the exponential relationship, and showed that, with specific values of  $A'$  and  $E_A$ , it would account for a number of other velocity coefficients, including, as we have seen, those for the hydrolysis of sucrose. He recognized the similarity of Hood's equation with the van't Hoff isochore, which connects the equilibrium constant,  $K$ , of a chemical reaction with the increase,  $\Delta E$ , in internal energy,

$$\ln K = \text{constant} - \frac{\Delta E}{RT}, \quad (3)$$

and by analogy suggested the existence of an equilibrium between 'passive' molecules of the reacting species and 'active' molecules formed from normal molecules by the absorption of energy. It had hitherto been difficult to understand why only a few molecules—rather than all of them—reacted at any given time. The answer given by Arrhenius is that only that small fraction of the total number of molecules which is active at any instant can react; chemical changes are not instantaneous because the distribution of energy requires time. The correctness of his view has since received overwhelming confirmation.

The superiority of the Hood-Arrhenius equation over the Harcourt-Esson and all other empirical relations lay in the fact that it not only fulfilled the object for which it was created—i.e. to summarize in

† *Phil. Trans.*, 186, 817, (1895); *ibid.*, 212, 187, (1913); see also, *ibid.*, 157, 132, (1867).

convenient form the relation between the velocity constant and temperature—but also threw light on the mechanism of chemical change. If we replace  $A'$  by  $\ln A$ , the equation can be rewritten in the form

$$k = Ae^{-E_A/RT}. \quad (4)$$

The fraction  $e^{-E_A/RT}$ , according to the Boltzmann distribution law, is proportional to the number of molecules possessing energy  $E_A$  in excess of the average energy characteristic of all the molecules at the temperature  $T$ . The Arrhenius equation, therefore, means that the number of molecules reacting per unit time is proportional to the number of molecules which are in a suitably activated condition. Processes other than chemical transformation obey the same law; for example:

the number of molecules of a liquid evaporating per second  
 $= \text{const.} \times e^{-L/RT}$  ( $L$  is the latent heat of vaporization),

and

the number of electrons emitted by incandescent solids per second  
 $= \text{const.} \times e^{-W/RT}$  ( $W$  is the thermionic work term).

The Arrhenius hypothesis brings reaction velocity into line with such formulae, for it may be expressed in the same way:

the number of molecules undergoing chemical change per second  
 $= \text{const.} \times e^{-E/RT}.$

$E$  is termed the energy of activation, the critical increment of energy, or simply the critical increment, and is experimentally determinable by plotting the logarithm of the velocity constant against the reciprocal of the absolute temperature: the slope of the line, multiplied by the gas constant  $R$  (1.9869 calories per degree) gives the value of  $-E$  in calories per gram molecule. It will become clear subsequently that the value of  $E$  obtained in this way is not always equal to the energy of activation, and has to be corrected in various ways. The necessity for introducing such modifications in no way detracts from the general truth of the Arrhenius hypothesis, which is that activation of some kind is a necessary step in all chemical changes which proceed with measurable velocity. This is the foundation of chemical dynamics.

A great scientist, no less than a great artist, sometimes draws a picture which may be true in general outline though wrong in detail; and this is the case with Arrhenius's delineation. It is now quite

clear that his simple equation is but an excellent first approximation to the truth, which is more nearly, but still inadequately, represented by the equation

$$\ln k = B' + C' \ln T - \frac{E}{RT}. \quad (5)$$

An equation of this form was first proposed, though on insufficient experimental evidence, by Kooij,<sup>†</sup> and was later generalized by Trautz.<sup>‡</sup> The vapour pressure, thermionic, and kinetic data are all more faithfully represented by equations of this form than by those in which the constant  $C'$  is assumed to be zero.

If for the constants  $B'$  and  $C'$  we write, respectively,  $\ln B$  and  $C/R$ , equation (5) may be recast in the form:

$$k = BT^{C/R} e^{-E/RT}. \quad (6)$$

Trautz's argument is, briefly, that a combination of the van't Hoff isochore

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}, \quad (7)$$

with Kirchhoff's equation

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_P dT, \quad (8)$$

leads, when  $\Delta C_P$  is constant, to the relationship

$$K = JT^{\Delta C_P/R} e^{-\Delta H_0/RT}, \quad (9)$$

which may be resolved into two kinetic equations, each resembling equation (6).

We shall but briefly pause to consider in what way active molecules differ from passive ones. One of the earliest explanations<sup>§</sup> was that active molecules could be identified with those which, according to Maxwell's law, have fast velocities. The energy of activation then becomes simply the excess kinetic energy possessed by those molecules which react. This view is, as we shall see, consistent with later theoretical developments, according to which a potential energy barrier must be surmounted before reaction takes place, and only those molecules which approach the barrier with sufficient momentum to reach the top can be regarded as active.

The acquisition of a critical energy is obviously only one of the conditions which must be fulfilled before molecules can undergo

<sup>†</sup> *Z. physikal. Chem.*, **12**, 155, (1893).

<sup>‡</sup> *Ibid.*, **66**, 496, (1908).

<sup>§</sup> Hans Goldschmidt, *Physikal. Z.*, **10**, 206, (1909).

chemical change. Most reactions in chemistry are those where two or more molecular types are converted simultaneously; a second condition must therefore be that molecules meet. In order to assess the probability of their meeting we must first learn something of molecular velocities and diameters.

The form given above (equation 3) to the van't Hoff isochore is not the most general one, because the term  $\Delta E$  is sometimes found to be a function of temperature. Its general form is

$$\Delta E = RT^2 \frac{d \ln K}{dT}. \quad (10)$$

We shall find it convenient to define the Arrhenius energy of activation† or the apparent energy of activation as follows:

$$E_A = RT^2 \frac{d \ln k}{dT}. \quad (11)$$

By so doing, we shall embrace his hypothesis in its widest implication, without committing ourselves to the integrated and restricted form in which it was first propounded. Equation (11) can be transformed into

$$E_A = -R \frac{d \ln k}{d(1/T)}. \quad (12)$$

By the Arrhenius energy of activation we shall always mean the value found, graphically or analytically, from the dependence of the logarithm of the velocity coefficient on the reciprocal of the absolute temperature.

On applying the Arrhenius equation, in this general, differential form, to equation (6), we see that

$$E_A = E + CT. \quad (13)$$

It must be left for experiment to decide whether, and in what way, the apparent energy of activation varies with respect to the temperature.‡

Arrhenius was as much interested in the physiological as in the physical implications of his hypothesis,§ and it is gratifying to note

† More strictly, the differentiation of  $\ln K$  must refer to a constant volume, whereas the differentiation of  $\ln k$  usually refers to a constant pressure. With this distinction we deal more fully in Chapter XI.

‡ On applying these considerations to equation (2), we obtain  $E_A = mRT$ , a result which, it may be stated in advance, has never been substantiated with positive values of  $m$ .

§ Arrhenius, *Immunochemistry*, Leipzig, (1907).

that, particularly in the hands of Crozier and Hoagland,<sup>†</sup> labour in this interesting field has by no means been neglected.<sup>‡</sup>

### *Molecular Velocities*

The velocity of a molecule is usually altered after each successive collision with another molecule. Its speed is increased or decreased according as the molecule which it meets is travelling in the same or in the opposite direction. At any particular instant, a few of the molecules in a system containing a large number are at rest: some move very rapidly: most of the molecules have a speed not very different from the average velocity ( $v$ ) or from the root mean square velocity ( $c$ ), which is the hypothetical velocity which each molecule would possess if the total kinetic energy were equally distributed among them. The following simple derivation shows how these quantities may be calculated. In a cube of length  $l$  containing  $N$  molecules travelling with velocity  $c$ , the molecules may be imagined as divided into three groups, each group moving to and fro in directions parallel with the sides of the cube. The number of molecules striking one side of the cube in one second is  $\frac{1}{2}N \cdot c/2l$ . The change of momentum due to each impact is  $2mc$ , hence the rate of change of momentum, or the force  $X$  acting on the wall, is  $\frac{1}{2}N(c/l)mc$ . The pressure, or force per unit area, is

$$P = \frac{X}{l^2} = \frac{1}{3} \frac{mNc^2}{l^3} = \frac{1}{3} \frac{mNc^2}{V};$$

hence  $PV = \frac{1}{3}mNc^2$ . For one gram molecule of a perfect gas,  $PV = RT$ , and  $mN = M$ , the molecular weight; so that  $RT = \frac{1}{3}Mc^2$ . The root mean square velocity may thus be determined from the molecular weight and the temperature:

$$c = \sqrt{\frac{3RT}{M}}. \quad (14)$$

When  $R$  is given the value of  $8.315 \times 10^7$  ergs/degree,  $c$  has the units

<sup>†</sup> *Handbook of General Experimental Psychology*, Clark University Press, Worcester, U.S.A., (1934).

<sup>‡</sup> See, for example, 'The Physiological Control of Judgments of Duration; Evidence for a Chemical Clock', Hoagland, *J. General Psychology*, **9**, 267, (1933); 'The Influence of Temperature on Nerve Impulses Arising Spontaneously in Abdominal Ganglia', L. Prosser, *J. General. Physiol.*, **19**, 65, (1935); 'The Respiration of the Newt', Pomerat and Zarrow, *J. Cell and Comp. Physiol.*, **9**, 397, (1937); 'Pacemaker Aspects of Rhythmic Activity in the Nervous System', Hoagland, *Cold Spring Harbour Symposia on Quantitative Biology*, **4**, 267, (1936); 'The Pacemakers of Human Brain Waves in Normals and in General Paretics', Hoagland, *Amer. J. Physiol.*, **116**, 604, (1936); *J. Cell and Comp. Physiol.*, **10**, 29, (1937).

of cm./second. It can readily be shown that the average velocity in space is  $v = c\sqrt{(8/3\pi)}$ , hence

$$v = \sqrt{\frac{8RT}{\pi M}}, \quad (15)$$

and that the average velocity,  $u$ , in a given direction is†

$$u = \sqrt{\frac{RT}{2\pi M}}. \quad (16)$$

### Molecular Diameters

In order to calculate collision frequencies in liquid systems, the diameters of the molecules must be known. This is not necessary in gaseous systems, where the collision number may be determined directly from a knowledge of the density and viscosity of the gas at any given temperature. The dimensions of some organic molecules have been determined from measurements of the viscosity of vapours.‡ For many purposes an accurate evaluation of the diameter of molecules is not required, and a round figure of  $5 \times 10^{-8}$  cm. may be used. When a closer estimate is required it may be assumed that the molecules in a liquid or a solid at low temperatures are closely packed spheres.  $N$  molecules then occupy  $N\sigma^3/\sqrt{2}$  c.c., and the diameter is related to the molecular volume (in c.c. per gram molecule) by the equation

$$\sigma = 1.33 \times 10^{-8} \times V_m^{1/3}. \quad (17)$$

Molecular diameters found in this manner are in quite good agreement with those afforded by the study of surface films and the reflection of X-rays from crystals. Propyl iodide may be taken as an example. From surface tension measurements a length of 4.70 Å. can be ascribed to the chain of carbon atoms.§ The radius of the iodine atom, according to the X-ray analysis of its crystal lattice, is 2.19 Å. We may therefore take 9.08 Å. as the approximate length of the molecule. Its breadth at the hydrocarbon end is  $\sqrt{20.7} = 4.55$  Å.|| At the iodine end, the breadth is 4.38 Å. The molecule of propyl iodide has thus an almost uniform thickness of 4.47 Å. and a length of 9.08 Å. The geometric mean of these, 6.37 Å., corresponds to the hypothetical diameter which the molecule would possess if it were

† See, for example, Tolman, *Statistical Mechanics*, p. 60, The Chemical Catalog Co., New York, (1927); Moelwyn-Hughes, *Physical Chemistry*, p. 63, Cambridge, (1940).

‡ Lowry and Nasini, *Proc. Roy. Soc.*, A, 123, 686, (1929).

§ Kosekewitsch and Uschakowa, *Z. physikal. Chem.*, A, 157, 188, (1931).

|| Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., Oxford, (1941); Rideal, *Surface Chemistry*, 2nd ed., Cambridge, (1930).

symmetrical. The diameter calculated from the molecular volume by means of equation (17) is 6.12 Å.

Though it might be thought an advantage to have still more precise values of  $\sigma$  for the purpose of comparing the rates of homologous reactions, we shall not further pursue the subject. The familiar term 'diameter', as far as it applies to molecules, stands for an obsolete, though useful, conception. What is required in our work is a knowledge of the distance apart of the centres of gravity of reacting molecules, and this distance, as we shall see later, emerges directly from the kinetic analysis of the rates of reactions, without appealing to other sources (p. 106). The term in the meantime may still be retained for the sake of convenience.

### *Molecular Collisions*

The average velocity of a molecule is determined by its mass and temperature, and does not depend on the state of aggregation of the system in which it finds itself. We therefore apply equations (15) and (16) directly to solute molecules.

1. *The Number of Collisions between Molecules of Solute and a Plane Surface.* Let us consider a solution containing  $n$  molecules of solute per c.c. The number of such molecules reaching unit area of a plane surface of the boundary in one second equals the number of molecules contained in a cylinder of length  $u$ , which is  $nu$ . The

number of collisions by solute molecules on an area  $S$  cm.<sup>2</sup> is, therefore,  $Snu$  per second. We thus have:†

$$Z = nS \sqrt{\frac{kT}{2\pi m}}, \quad (18)$$

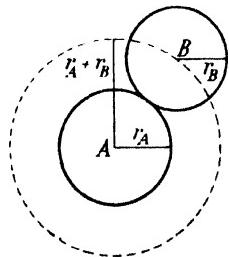
where  $m$  is the mass of one molecule and  $k$ , the Boltzmann constant, is  $1.372 \times 10^{-16}$  erg per degree.

FIG. 1.

### *2. The Number of Collisions between Molecules of Solute.*

We next require to know how many collisions occur in unit volume and unit time between two different kinds of solute molecules. Let there be  $n_A$  molecules of one kind and  $n_B$  molecules of the other kind per c.c., and let their radii be  $r_A$  and  $r_B$  respectively. We shall first find how many molecules of the  $B$  type collide with one molecule of the  $A$  type. The number per second is clearly (Fig. 1)

† Hertz, *Wied. Ann.*, 17, 177, (1882).



the number of  $B$  molecules the centres of which reach the surface of area  $4\pi(r_A+r_B)^2$  surrounding the  $A$  molecule. According to the formula of the preceding section, this number is

$$_1Z_B = n_B 4\pi(r_A+r_B)^2 \sqrt{\frac{kT}{2\pi\mu}}, \quad (19)$$

where  $\mu$ , the reduced mass, is defined by the equation

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}. \quad (20)$$

The total number of collisions per c.c. per second is just  $n_A$  times as great, so that

$$_A Z_B = n_A n_B (r_A+r_B)^2 \left\{ 8\pi kT \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right\}^{\frac{1}{2}}. \quad (21)$$

When one molecule is much larger than the other, this expression reduces to  $n_A n_B r_A^2 (8\pi kT/m_B)^{\frac{1}{2}}$ , i.e. the area is determined by the voluminous molecule and the velocity by the compact one.

More accurate derivations of these formulae have been frequently given.†

3. *The Number of Collisions between Molecules of Solute and Molecules of Solvent.* It is not so easy to determine the frequency of collisions between molecules of solute and molecules of solvent, to which, in many reactions, we have reason to suppose that the rate of chemical change is proportional. The reason is that an increase in temperature influences the number of collisions in two ways. In the first place, by increasing the average velocity of the molecules, it favours the collision frequency. In the second place, by increasing the free space in the solution, it adversely affects the collision frequency. The latter effect is the greater and, therefore, the net effect of an increase in temperature is to decrease the number of collisions made per second between a solute molecule and the solvent molecules which surround it.

On treating interdiffusion in liquids by the method used to treat self-diffusion in gases, the same equation is found to connect the coefficient,  $D$ , of diffusion, with the average velocity,  $v$ , and the mean free path,  $\lambda$ , in the two systems:‡

$$D = \frac{1}{3} \lambda v. \quad (22)$$

† e.g. Tolman, *Statistical Mechanics*, p. 67, Reinhold Publishing Co., New York, 1937; Moelwyn-Hughes, *Physical Chemistry*, p. 72, Cambridge, (1940).

‡ Riecke, *Z. physikal. Chem.*, **6**, 564, (1890).

The total number of solvent molecules encountered per second by one solute molecule is

$$_1Z_S = \frac{v}{\lambda} = \frac{v^2}{3D} = \frac{8RT}{3\pi M_1 D}. \quad (23)$$

To make an approximate allowance for a tendency of the velocity to persist after collision, a term  $1.051/(1-\theta)$  may be introduced.<sup>†</sup>  $\theta$  depends on the masses of the colliding molecules and is roughly equal to  $M_1/(M_1 + M_S)$ , where  $M_1$  is the molecular weight of the solute and  $M_S$  that of the solvent. Hence, to within a few per cent.,

$$_1Z_S = \frac{8RT}{3\pi D} \left( \frac{M_1 + M_S}{M_1 M_S} \right). \quad (24)$$

This equation was derived by Jowett,<sup>‡</sup> who employed it to calculate collision frequencies in aqueous solutions from a knowledge of the diffusion coefficients. He recognized the implication that  $_1Z_S$  diminishes with increase in temperature, but made, however, no attempt to test it.

The frequency of collisions between solute and solvent molecules has been calculated in another way, starting from the expression§ for the average value of the square of the displacement,  $\bar{\Delta x^2}$ , suffered by a spherical particle of radius  $r$  in time  $t$  when in a medium of viscosity  $\eta$ :

$$\bar{\Delta x^2} = \frac{kTt}{3\pi\eta r}. \quad (25)$$

The displacement is in one dimension only. Now the average value of the square of the velocity in a given direction of a particle of mass  $m$  we have seen to be

$$\bar{u^2} = \frac{kT}{m}. \quad (26)$$

Hence

$$\frac{\bar{\Delta x^2}}{\bar{u^2}} = \bar{t^2} = \frac{2mt}{3\pi\eta\sigma}. \quad (27)$$

There can be no formal justification for equating the average time to the square root of the average of the square of the time, but the risk, having once been taken, has at least led to no disaster. Then

$$t = \frac{2m}{3\pi\eta\sigma},$$

and

$$_1Z_S = \frac{1}{t} = \frac{3\pi\eta\sigma}{2m}. \quad (28)$$

<sup>†</sup> Jeans, *The Dynamical Theory of Gases*, p. 260, 4th ed., Cambridge, (1925).

<sup>‡</sup> *Phil. Mag.*, 8, 1059, (1929). An alternative derivation is given by Syrkin, *Acta Physicochim. U.S.S.R.*, 1, 855, (1935).    § Einstein, *Z. Elektrochem.*, 14, 235, (1908).

This expression<sup>†</sup> requires no knowledge of the coefficient of diffusion and is the one which has consequently been most frequently applied to the kinetics of reactions involving solute-solvent collisions.

One of the most promising theories of the viscosity of liquids<sup>‡</sup> has furnished an expression for intermolecular frequencies which, apart from an insignificant numerical factor, is the same as that obtained here by an adaptation of Einstein's theory of diffusion.

We shall occasionally require to know the frequency of collisions between a solute molecule and solvent molecules in which a second solute molecule is present. The number of collisions per c.c. per second between  $n_A$  solute molecules of type *A* and solvent molecules is, from equation (28),  $3\pi\eta n_A r_A/m_A$ , where  $n_A$ ,  $r_A$ , and  $m_A$  are, respectively, the concentration, radius, and mass of molecules of type *A*. The chance that a molecule of a second solute, of type *B*, shall be present, may be taken as the molar fraction  $n_B/(n_A+n_B+n_S)$ , where  $n_S$  is the number of solvent molecules per c.c. As an average expression for the frequency of binary collisions between solute molecules of comparable dimensions in which a solvent molecule is present, we then have<sup>§</sup>

$${}_A Z_B = \frac{3\pi\eta}{4} \left( \frac{n_A n_B}{n_A + n_B + n_S} \right) (r_A + r_B) \left( \frac{1}{m_A} + \frac{1}{m_B} \right), \quad (29)$$

which, for dilute solutions, is nearly

$${}_A Z_B = \frac{3\pi\eta}{4} \frac{n_A n_B}{n_S} (r_A + r_B) \left( \frac{1}{m_A} + \frac{1}{m_B} \right). \quad (30)$$

In order to apply equations (28) and (30) we shall require a knowledge of the viscosities of various liquids at different temperatures. For this purpose a few data (Table 1), collected from the literature, have been cast in an equation of the form first suggested by de Guzman,<sup>||</sup> which is

$$\eta = ae^{B/RT}. \quad (31)$$

If molecules of solute and solvent were to repel each other with a force, *X*, which is inversely proportional to the fifth power of their distance, *a*, apart,

$$X(a) = Aa^{-5}, \quad (32)$$

<sup>†</sup> Moelwyn-Hughes, *Trans. Chem. Soc.*, 95, (1932).

<sup>‡</sup> Andrade, *Phil. Mag.*, 17, 497, (1934).

<sup>§</sup> Moelwyn-Hughes, *Phil. Mag.*, 14, 112, (1932).

<sup>||</sup> *Anales de la Sociedad Española de Física y Química*, 1913; see Andrade, *loc. cit.*

Table 1  
*The Viscosities of Certain Liquids*

$$\eta = ae^{B/RT}$$

Liquid	$\eta_{25^\circ\text{C.}}$ (gm./cm. sec.)	$a$ (gm./cm. sec.)	$B$ (calories/gram mole)	
CHCl <sub>3</sub>	$5.50 \times 10^{-3}$	$5.62 \times 10^{-4}$	$1,350 \pm 240$	
(CH <sub>3</sub> ) <sub>2</sub> CO	$3.16 \times 10^{-3}$	$2.12 \times 10^{-4}$	$1,600 \pm 60$	
nC <sub>6</sub> H <sub>14</sub>	$3.12 \times 10^{-3}$	$1.218 \times 10^{-4}$	$1,660 \pm 5$	
CCl <sub>4</sub>	$9.21 \times 10^{-3}$	$1.664 \times 10^{-4}$	$2,375 \pm 5$	
C <sub>2</sub> H <sub>5</sub> Cl <sub>2</sub>	$1.64 \times 10^{-2}$	$1.047 \times 10^{-4}$	$2,990 \pm 30$	
CH <sub>3</sub> OH	$5.56 \times 10^{-3}$	$8.65 \times 10^{-5}$	$2,465 \pm 40$	
C <sub>2</sub> H <sub>5</sub> OH	$1.10 \times 10^{-2}$	$4.65 \times 10^{-5}$	$3,225 \pm 130$	
nC <sub>3</sub> H <sub>7</sub> OH	$1.98 \times 10^{-2}$	$1.46 \times 10^{-5}$	$4,270 \pm 280$	
CH <sub>3</sub> COOH	$1.15 \times 10^{-2}$	$1.305 \times 10^{-4}$	$2,650 \pm 40$	
C <sub>6</sub> H <sub>6</sub>	$6.06 \times 10^{-3}$	$4.915 \times 10^{-5}$	$2,850 \pm 240$	
C <sub>6</sub> H <sub>5</sub> .CH <sub>3</sub>	$5.54 \times 10^{-3}$	$1.515 \times 10^{-4}$	$2,130 \pm 20$	
C <sub>6</sub> H <sub>5</sub> .COCH <sub>3</sub>	$1.67 \times 10^{-2}$	$1.09 \times 10^{-4}$	$2,980 \pm 640$	
C <sub>6</sub> H <sub>5</sub> .NO <sub>2</sub>	$1.87 \times 10^{-2}$	$1.10 \times 10^{-4}$	$3,040 \pm 170$	
C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> OH	$5.01 \times 10^{-3}$	$7.16 \times 10^{-6}$	$5,240 \pm 440$	
C <sub>6</sub> H <sub>5</sub> .NH <sub>2</sub>	$3.66 \times 10^{-2}$	$6.56 \times 10^{-6}$	$5,330 \pm 10$	
H <sub>2</sub> O	$\begin{cases} (0^\circ\text{ C.}) \\ (25^\circ\text{ C.}) \\ (50^\circ\text{ C.}) \end{cases}$	$\begin{cases} 1.79 \times 10^{-2} \\ 8.94 \times 10^{-3} \\ 5.50 \times 10^{-3} \end{cases}$	$\begin{cases} 1.53 \times 10^{-6} \\ 1.006 \times 10^{-6} \\ 2.463 \times 10^{-6} \end{cases}$	$\begin{cases} 5,080 \\ 4,020 \\ 3,470 \end{cases}$

the coefficient of diffusion would be†

$$D = \frac{kT}{2.66(n_1+n_S)\sqrt{\left(\frac{1}{A}\left(\frac{1}{m_1} + \frac{1}{m_S}\right)\right)}}. \quad (33)$$

On combining with equation (24), we see that the number of collisions made per second between one solute molecule and the solvent molecules is

$${}_1Z_S = \frac{n_1+n_S}{\pi} \sqrt{\left(\frac{8}{3} A \left(\frac{1}{m_1} + \frac{1}{m_S}\right)\right)}. \quad (34)$$

Unfortunately, few molecules, if any, obey this law of repulsion.

### *The Origin of the Collision Theory*

The rate,  ${}_A Z_B$ , at which molecules collide is known in terms of the temperature, the molecular diameters, and the molecular weights. The fractional number of molecules possessing an energy  $E$  is proportional to  $e^{-E/RT}$ ; hence the rate at which molecules collide while possessing an energy  $E$  is proportional to the product  ${}_A Z_B e^{-E/RT}$ , and may sometimes be equal to it. A comparison of the computed rate and the observed rate of gaseous reactions was first made by

† Langevin, *Ann. de Chim. et de Phys.*, 5, 245, (1905).

Trautz,<sup>†</sup> who found, for the few bimolecular reactions then known, quite reasonable agreement. He therefore concluded that

### The rate of bimolecular gas reactions

$$= \text{The rate of collisions} \times e^{-E/RT}. \quad (35)$$

Using equation (21), we can then write

$$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = n_A n_B (r_A + r_B)^2 \left\{ 8\pi k T \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right\}^{\frac{1}{2}} \times e^{-E/RT}.$$

The same important result was independently reached by W. C. McC. Lewis,<sup>‡</sup> to whom, on account of the war of 1914–18, Trautz's publication was not available, and later by many others of whom the same cannot be said. This equation represents the simplest formulation of the collision theory.

Its first application to reactions in solution§ met with less success, and it seemed that the theory was not sufficient, without major modifications, to account for the rate of bimolecular reactions in solution. The erroneous view was, consequently, for some time held that it was applicable to gas reactions but inapplicable to reactions in solution. The position in 1929|| was that the phenomena of chemical change which then offered some prospect of interpretation in terms of the kinetic theory were confined to gaseous systems. Chemical change, however, is fundamentally the same in all states of matter, and the belief persisted that either the success of the collision theory as applied to gases was fortuitous or that, if it were genuine, it should spread to solutions also. In point of fact, equation (35) tallies excellently with some of the most precise data that we possess on the velocity of chemical change in solution,<sup>††</sup> but it is only relatively recently that this was pointed out.<sup>‡‡</sup> The apparent distinction between the kinetics of reactions in the two phases is now known to be due, not to the failure of the theory but to the paucity of data by which it had been tested in both phases. In 1929 no reactions in solution were known which fitted into equation (35); six out of the seven known gas reactions did. In 1933 over one hundred reactions

<sup>†</sup> *Z. anorg. Chem.*, **96**, 1, (1916).

<sup>‡</sup> *Trans. Chem. Soc.*, **113**, 471, (1918).

<sup>§</sup> Christiansen, *Z. physikal. Chem.*, **113**, 35, (1924).

<sup>||</sup> Cf. Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, 2nd ed., Oxford, (1929).

<sup>††</sup> Hecht and Conrad, *Z. physikal. Chem.*, **3**, 450, (1889).

<sup>‡‡</sup> Moelwyn-Hughes, *Chem. Rev.*, **10**, 241, (1932); *Phil. Mag.*, **vii**, **14**, 112, (1932).

in solution had been revealed which coincided with equation (35) and quite a high proportion of gas reactions had been found which did not.

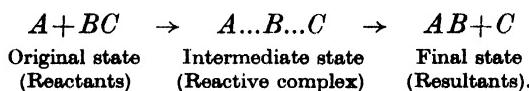
It is doubtless inevitable, and perhaps instructive, that knowledge should advance in this step-wise manner, zigzagging, as it were, about the high road of truth.

### *The Calculation in Absolute Magnitude of the Velocity of Chemical Reaction*

The velocity of chemical change depends, as we have seen, on at least two factors, namely, the rate at which molecules meet and the chance that they should have the requisite energy. The former quantity can, despite a slight uncertainty about the magnitude of the molecular 'diameter', be assessed within fairly narrow margins. The latter quantity is proportional to, and, in certain specialized cases, exactly equal to, the Boltzmann factor  $e^{-E/RT}$ . In our discussion so far we have made use of values of  $E$  determined kinetically. Clearly, if we can evaluate  $E$  independently of kinetic sources, we have achieved one of the main objects of chemical kinetics (p. 1). Heitler and London† showed how this could be done. Let us consider the chemical conversion of an atom,  $A$ , and a molecule,  $BC$ , into an atom,  $C$ , and a molecule,  $AB$ :



The conversion takes place, it is known, through the intermediate formation of an atomic configuration of high symmetry,‡ and we may depict the change to be as follows:



As reaction proceeds, there is a gradual loosening of the ties between atoms  $B$  and  $C$  and a gradual strengthening of the ties between atoms  $A$  and  $B$ . In the intermediate stage, the atoms  $A$  and  $C$  influence the central atom,  $B$ , with comparable effects, and, if they are identical, with equal effects. The interaction energy of atoms  $A$  and  $B$  can be represented as a function of the distance,  $r_{AB}$ , between them. Similarly, the interaction energy of atoms  $B$  and  $C$  can be represented as a function of  $r_{BC}$ ; and the energy of interaction of the distant atoms,  $A$  and  $C$ , can be expressed as a function of  $r_{AC}$ .

† *Z. Physik*, **44**, 457, (1927).

‡ Lowry, *Trans. Chem. Soc.*, **828**, (1923).

which, if the combination is a linear one, is clearly equal to the sum of  $r_{AB}$  and  $r_{BC}$ . The net effect of the three interactions is to afford a dependence of the total energy,  $E$ , on a reaction coordinate,  $r$ , such as is shown in Fig. 2. The energy of activation is seen to be the

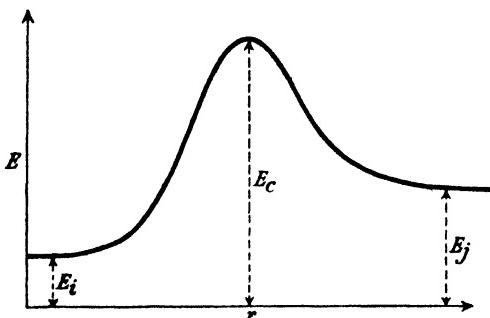


FIG. 2.

difference between the energy of the critical and the original atomic configurations. For the forward reaction ( $A + BC \rightarrow AB + C$ ), the critical increment is

$$E_1 = E_c - E_i \quad (36)$$

and for the reverse reaction ( $AB + C \rightarrow A + BC$ ), the critical increment is

$$E_2 = E_c - E_j. \quad (37)$$

The gain,  $\Delta E$ , in internal energy associated with the reaction, which equals the heat absorbed at constant volume, is then

$$\Delta E = E_1 - E_2 = E_j - E_i. \quad (38)$$

In these considerations we are neglecting the difference between the free energy and the total internal energy, which is strictly valid only at the absolute zero of temperature.

An ideal reaction for testing the theory of Heitler and London is afforded by the conversion of ortho-hydrogen into para-hydrogen, the isolation of which was effected by Bonhoeffer and Harteck.† A kinetic examination of the conversion‡ showed it to proceed by the following mechanism:



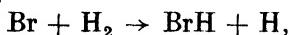
To the evaluation of the energy of activation of this reaction, Eyring and Polanyi§ successfully applied the new theory, and thereby

† *Z. physikal. Chem.*, **B**, 4, 113, (1929).

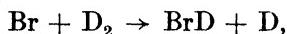
‡ A. Farkas, *ibid.*, **B**, 10, 419, (1930).

§ *Ibid.*, **B**, 12, 279, (1931).

achieved for the first time the calculation in absolute magnitude of the velocity of a chemical reaction. The reactions of the bromine atom with hydrogen,<sup>†</sup>



and with deuterium,<sup>‡</sup>



proceed by the same mechanism, and the comparison between the observed and calculated energies of activation is, if anything, still closer. Thus, the experimental value of  $E$  for the reaction between the bromine atom and the hydrogen molecule is 21,150 calories, while the calculated value is 22,100 calories.<sup>§</sup> With the details of the theory—important and interesting as they are—we cannot here deal,<sup>||</sup> as their proper province is the study of the kinetics of chemical change in gaseous systems, where complications due to the presence of the solvent are absent. Some remarks on statistical derivations of kinetic formulae are made in Appendix I; they refer to unitary chemical processes which, in solution at least, appear to be the exception rather than the rule.

### *Synchronization in Chemical Kinetics*

An outstanding feature of the kinetics of reactions in solution is the comparative rarity of unitary processes. The simple chemical change represented by the union of molecules  $A$  and  $B$  to form a third molecule  $AB$  is often found in practice to be accompanied by the reverse reaction, from which, in theory, it can never be entirely divorced. Moreover, while waiting for the final state to be reached, molecules  $A$  and  $B$  may to some extent fail to bear the strain, and break down into smaller fragments, or react with solvent molecules. Nor is this all. Quite often, molecules  $A$  and  $B$  do not form their product,  $AB$ , directly, but do so through the intermediate formation of another molecule,  $C$ , which, though not stable enough to be isolated, unmistakably signifies its existence by physical properties such as infra-red absorption bands or optical rotatory power. Seldom,

<sup>†</sup> Bodenstein and Luetkemeyer, *Z. physikal. Chem.*, **114**, 208, (1925).

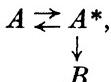
<sup>‡</sup> Bach, Bonhoeffer, and Moelwyn-Hughes, *ibid.*, **B**, **27**, 71, (1934).

<sup>§</sup> Moelwyn-Hughes, *Ann. Reports, Chem. Soc.*, p. 92, (1935); cf. 25,100 calories calculated by Wheeler, Topley, and Eyring, *J. Chem. Physics*, **3**, 178, (1935).

<sup>||</sup> See Polanyi, *Atomic Reactions*, Williams and Norgate, London, (1932); Glasstone, Eyring, and Laidler, *The Theory of Rate Processes*, McGraw-Hill Book Co., New York, (1941); Heitler, *Elementary Wave Mechanics*, Oxford, (1945); Moelwyn-Hughes, *Physical Chemistry*, chap. xi, Cambridge, (1940).

in fact, does a reaction in solution take place without the accompaniment of another. Nature, it would seem, prefers to bring about material changes through a concerted set of reactions rather than through one elementary reaction. Chords are more often struck than musical notes. While the statistical treatments of recent years have been largely directed to the difficult task of analysing the timbre of pure notes, the methods of chemical kinetics are still the only ones available for the equally difficult task of picking out the notes in a chord.

It would thus appear that the laws of chemical change, while putting considerable inducement on a molecule to behave in a certain way, always leave it a loophole to act in another way. The idea is implicit in the original hypothesis of Arrhenius, for, in the familiar scheme



the active molecule,  $A^*$ , is given the option of reverting into the normal molecule,  $A$ , which it generally chooses, or of passing into product molecules,  $B$ . Most of the reactions with which we have to deal, therefore, proceed with a net velocity which is due to the synchronization of at least two rates, and we must agree on a simple yet satisfactory method of dealing with the situation.

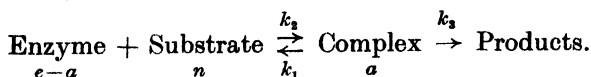
The hypothesis of the stationary state of intermediaries, introduced by Bodenstein<sup>†</sup> to explain what then appeared to be kinetic abnormalities, and formally developed by Christiansen and Kramers,<sup>‡</sup> will be found sufficient for most of our needs. A stationary concentration of molecules of the intermediate compound is said to have been reached when the number formed, per unit volume and time, equals the number destroyed:

$$\left( \frac{da}{dt} \right)_s = 0. \quad (39)$$

This conception we shall now apply to a variety of simple problems.

#### *Applications of the Stationary State Hypothesis*

1. *Enzyme Reactions.* Let us consider an enzyme of concentration  $e$  molecules per c.c., to combine with a substrate of concentration  $n$ , forming a complex of concentration  $a$ , as in the following scheme:



<sup>†</sup> *Z. physikal. Chem.*, **85**, 329, (1913).

<sup>‡</sup> *Ibid.*, **104**, 451, (1923).

The rate at which the complex is formed is

$$+\frac{da}{dt} = k_2(e-a)n - k_1a - k_3a.$$

According to equation (39), its stationary concentration is

$$a = \frac{k_2 en}{k_2 n + (k_1 + k_3)},$$

and the velocity of chemical change is consequently

$$v = k_3 a = \frac{k_3 k_2 en}{k_2 n + (k_1 + k_3)}. \quad (40)$$

The limiting value,  $V$ , of this velocity is clearly  $k_3 e$ ; hence, writing  $K$  for  $(k_1 + k_3)/k_2$  we have

$$\frac{v}{V} = \frac{n}{n+K}. \quad (41)$$

We see that  $K$  is numerically equal to the concentration,  $n'$ , of substrate at which the reaction velocity is one-half of its limiting value,  $V$ . This constant is known as the Michaelis constant† and is one of the most important properties of enzyme systems.‡

When the stationary concentration of complex is small compared with the amount of catalyst, somewhat simpler relations of the same form ensue.§

*2. Gas Reactions.* Let us now suppose that active molecules are formed by collisions between normal molecules, and are then given the option of losing their energy of activation by collisions with normal molecules or of decomposing into products. The rate of production of active molecules is then

$$\frac{da}{dt} = k_2 n^2 - k_4 na - k_3 a. \quad (42)$$

Using the same method as before to determine the stationary concentration, we obtain, for the rate of chemical change,

$$-\frac{dn}{dt} = \frac{k_3 k_2 n^2}{k_4 n + k_3}. \quad (43)$$

† Michaelis and Menten, *Biochem. Z.*, **49**, 333, (1913).

‡ See Euler, *Chemie der Enzyme*, vols. i and ii, Munich, (1927); Haldane, *Enzymes*, London, (1930); *Ergebnisse der Enzymforschung*, edited by Nord and Weidenhagen, Leipzig, (1932 onwards).

§ Langmuir, *J. Amer. Chem. Soc.*, **38**, 2221, (1916).

At high concentrations, therefore, the reaction is apparently a unimolecular one, for then

$$-\frac{dn}{dt} = \left(\frac{k_3 k_2}{k_1}\right)n,$$

and at low concentrations the reaction is bimolecular:

$$-\frac{dn}{dt} = k_2 n^2.$$

It is according to this mechanism that many organic compounds, and certain inorganic compounds, such as nitrogen pentoxide, decompose in the gaseous state.<sup>†</sup>

The ratio of the velocity,  $v$ , at a molecular concentration,  $n$ , to the limiting velocity,  $V$ , is now seen to be:

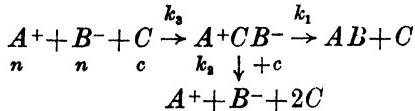
$$\frac{v}{V} = \frac{n}{n + (k_3/k_4)}, \quad (44)$$

and the concentration,  $n'$ , corresponding to one-half of the limiting velocity is

$$n' = k_3/k_4. \quad (45)$$

This concentration, like the bimolecular velocity coefficient  $k_2$ , is a specific property of the reaction, and varies from about  $10^{-6}$  gram-moles per litre in the case of nitrogen pentoxide to about  $10^{-2}$  gram-moles per litre in the case of dimethyl ether. Oxygen molecules are several thousands of times more efficient than helium atoms in quenching the resonance radiation of mercury atoms, so that we may expect the deactivation constant,  $k_4$ , also to be highly specific.

3. *Reactions between Charged Particles.* Ions of opposite charge (and of equal concentrations,  $n$ ) do not unite on collision in the gas phase unless a third particle (of concentration  $c$ ) is present to stabilize the union by withdrawing some of the energy released. We may well postulate the existence of a ternary complex, which can either revert to its antecedent molecules or pass over into products:



<sup>†</sup> Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, 3rd ed., Oxford, (1933); Kassel, *The Kinetics of Homogeneous Gas Reactions*, The Chemical Catalog Co., New York, (1932); Schumacher, *Chemische Gasreaktionen*, Steinkopff, Dresden and Leipzig, (1938).

The rate at which such intermediaries are formed is

$$+\frac{da}{dt} = k_3 n^2 c - k_2 c a - k_1 a.$$

Hence, as in the preceding sections, the rate of reaction becomes

$$-\frac{dn}{dt} = \frac{k_1 k_3 c n^2}{k_2 c + k_1}, \quad (46)$$

which gives us a termolecular change at low concentrations,

$$-\frac{dn}{dt} = k_3 c n^2, \quad (47)$$

and an apparently bimolecular one at high concentrations,

$$-\frac{dn}{dt} = \left(\frac{k_1 k_3}{k_2}\right) n^2. \quad (48)$$

Most of the facts established in connexion with the rate of union of ions in gases† can be explained on this basis,‡ though alternative mechanisms, to be discussed later (p. 114), have been also advanced.

Increasing the concentration alters the mechanism of an enzyme reaction from one of the first order to one of zero order, the mechanism of a gas reaction from one of the second order to one of the first order, and the mechanism of ionic union in the gas phase from one of the third order to one of the second order. These generalities are illustrated in Fig. 3.

4. *Chain Reactions.* Up to the present, no role has been ascribed to the products of reaction. If active molecules of reactants (of concentration  $a$ ) alone undergo chemical change, they must yield, primarily, active molecules of products (of concentration  $a'$ ). Let it now be assumed that these are capable of generating new molecules of reactants by collisions with ordinary molecules (of concentration  $n$ ). The rate of production of active reactants is then obtained by adding one term to equation (42), which becomes

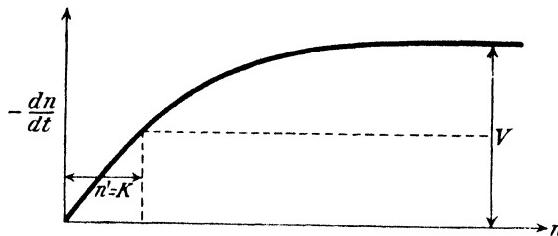
$$\frac{da}{dt} = k_2 n^2 + \alpha k_3 n a' - k_3 a - k_4 n a. \quad (49)$$

The terms, in order, denote (1) formation by collisions between

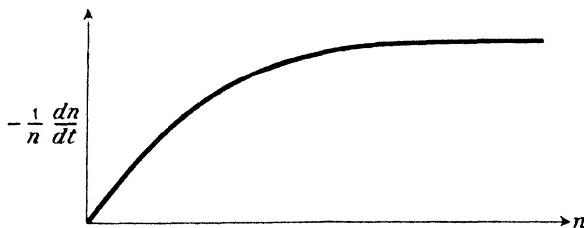
† J. J. Thomson and G. P. Thomson, *The Conduction of Electricity Through Gases*, 3rd ed., Cambridge, (1928).

‡ Moelwyn-Hughes, *Trans. Faraday Soc.*, **34**, 91, (1938).

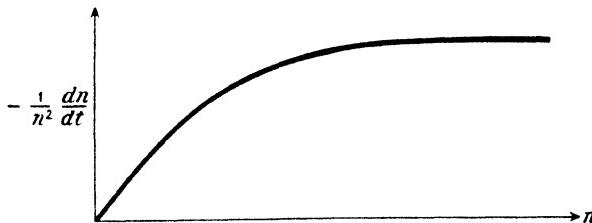
normal molecules, (2) formation by collisions between normal reactants and active products, (3) destruction by chemical con-



Rate ( $-dn/dt$ ), initially proportional to the concentration,  $n$ , becomes later independent of it. Examples: Enzyme reactions, other than oxidations, and certain surface-catalysed reactions.



Rate ( $-dn/dt$ ), initially proportional to  $n^2$ , becomes later proportional to  $n$ . Examples: Decomposition of nitrogen pentoxide and of certain organic compounds in the gaseous phase.



Rate ( $-dn/dt$ ), initially proportional to  $n^3$  becomes, at higher concentrations, proportional to  $n^2$ . Example: The neutralization of electrical charges on gaseous particles.

FIG. 3. The influence of concentration on the velocity of chemical change.

version, and (4) destruction in deactivating collisions with ordinary molecules. The rate at which active molecules of products are formed is

$$\frac{da'}{dt} = k_3 a - k_6 na'. \quad (50)$$

The important term,  $\alpha$ , takes account of the fact that not all those collisions which are effective in deactivating reactive products are fruitful in generating active reactants. On applying the stationary state hypothesis to both equations (49) and (50), we have

$$\alpha = \frac{k_2 n^2}{k_4 n + k_3(1-\alpha)}$$

and, therefore, 
$$-\frac{dn}{dt} = \frac{k_2 n^2}{(k_4/k_3)n + (1-\alpha)}. \quad (51)$$

When  $\alpha$  is zero, the reaction is termed a thermal one and we recover the formulae of section 2: when  $\alpha$  has a real value, the reaction is said to be a chain one. When  $\alpha$  exceeds unity, the denominator in equation (51) may become very small, or even zero, and the rate of reaction consequently may become very large, or even infinite. The latter contingency corresponds to an explosion.

This interpretation forms the basis of current theories of explosive reactions in gases† and of oxidative enzyme reactions in solution.‡

#### *Activation among many Degrees of Freedom*

It has already been emphasized that the fractional number ( $dN/N$ ) of molecules possessing energy  $E$ , though always proportional to the Boltzmann factor  $e^{-E/RT}$ , is exactly equal to it only under certain special conditions, into which we must now look more closely.

Only when the molecular energy can be expressed as the sum of two square terms is the fractional number of molecules possessing energy  $E$  exactly equal to the Boltzmann factor. Now suppose the energy of activation were made up of a kinetic contribution  $\frac{1}{2}m_1 u_1^2$  from one molecule, and a similar contribution  $\frac{1}{2}m_2 u_2^2$  from another molecule, then, for the pair, we should have

$$\epsilon = \frac{1}{2}m_1 u_1^2 + \frac{1}{2}m_2 u_2^2,$$

which clearly consists of two square terms. Or suppose, in the second place, that the energy of activation were accommodated completely in a single harmonic oscillator, for which the energy is

$$\epsilon = \frac{1}{2}fx^2 + \frac{1}{2}\mu x^2,$$

where  $x$  is the displacement from the equilibrium position,  $f$  the

† Semenoff, *Chemical Kinetics and Chain Reactions*, Oxford, (1935); Hinshelwood and Williamson, *The Reaction between Hydrogen and Oxygen*, Oxford, (1934).

‡ Moelwyn-Hughes, *Acta Physicochimica, U.S.S.R.*, 3, 593, (1935).

restoring force constant,  $\mu$  the reduced mass, and  $\dot{x}$  the velocity. Here again, we are using only two square terms—one for the potential energy and one for the kinetic energy of the oscillator. The success of the collision theory in the simple form tested by Trautz is doubtless due to the nearness of these models to the systems examined.

The more familiar expressions of Boltzmann for the distribution of energy refer to ideal gases, for which the energy is entirely kinetic, and consists of three square terms, one associated with the motion resolved along each of the three coordinate axes:

$$\epsilon = \frac{1}{2}m(u^2 + v^2 + w^2).$$

There is no reason to suppose that the activation of molecules in general is restricted to energies which can be expressed as three square terms. On the other hand, there are many reasons for supposing that internal molecular motions, such as the harmonic oscillation discussed above, can also contribute to it. The general form of the distribution law, when the energy of the molecules is expressible as the sum of  $2s$  square terms is

$$\frac{dN}{N} = \frac{1}{\Gamma(s)} e^{-E/RT} \left(\frac{E}{RT}\right)^s \frac{dE}{E}. \quad (52)$$

This expression gives the number,  $dN$ , of molecules which, out of a total number,  $N$ , possess energies lying between  $E$  and  $E+dE$ , when the energy per molecule can be expressed as the sum of  $2s$  square terms. It was derived by Berthoud in a series of notable papers† which have been completely overlooked. Many later and independent derivations of the same formula have therefore appeared.‡ The expression may be regarded either as the fraction of the total number of molecules,  $dN/N$ , possessing an energy within the limits  $E$  and  $E+dE$ , or as the probability,  $dP$ , that any molecule chosen at random shall possess energies within the same limits. The chance that a molecule shall possess an energy greater than  $E$  is

† *J. Chim. Phys.*, **9**, 352, (1911); *ibid.*, **10**, 573, (1912); *ibid.*, **11**, 577, (1913); *ibid.*, **12**, 564, (1914). I have altered the notation only, so as to conform to later usage, by making the obvious substitutions  $E = C_v \tau$  and  $s = C_v/R$ .

‡ Polanyi, *Z. Physik*, **1**, 337, (1920); Herzfeld, *Müller-Pouillet Lehrbuch der Physik*, III, 2, *Kinetische Theorie der Wärme*, p. 201, Braunschweig, (1925); G. N. Lewis and D. F. Smith, *J. Amer. Chem. Soc.*, **47**, 1508, (1925); Christiansen, *Proc. Camb. Phil. Soc.*, **23**, 438, (1926); Hinshelwood, *Proc. Roy. Soc. A*, **113**, 230, (1926); Fowler and Rideal, *ibid.*, p. 570.

obtained by integrating  $dP$  with respect to  $E$ , from the lower limit of  $E$  to the higher limit of infinity:

$$\begin{aligned} P &= \int_E^\infty dP = \int_E^\infty \frac{E^{s-1}}{(RT)^s} \frac{e^{-E/RT}}{\Gamma(s)} dE \\ &= e^{-E/RT} \left[ \frac{(E/RT)^{s-1}}{(s-1)!} + \frac{(E/RT)^{s-2}}{(s-2)!} + \dots + 1 \right]. \end{aligned} \quad (53)$$

When  $s$  is 1, that is, when two square terms suffice to define the energy,  $P$  reduces to  $e^{-E/RT}$ , as indicated above. When  $s$  is 2, we have

$$P = e^{-E/RT} \left( \frac{E}{RT} + 1 \right). \quad (54)$$

The series is a diminishing one. In many chemical reactions  $E/RT$  is large, and a good approximation to the ratio of the number of molecules possessing energy  $E$  or more to the total number is obtained by omitting all terms except the first one, when

$$P = \frac{dN}{N} \doteq e^{-E/RT} \frac{(E/RT)^{s-1}}{(s-1)!}. \quad (55)$$

If we now assume that two square terms represent the kinetic energies of a pair of colliding molecules, and that each of the internal modes of motion can also be represented as the sum of two square terms, then the number,  $F$ , of internal modes of motion, or degrees of freedom, is  $F$ , where

$$F = s - 1. \quad (56)$$

The chance that two molecules in collision shall possess an energy not less than  $E$  is thus approximately

$$e^{-E/RT} \frac{(E/RT)^F}{F!}. \quad (57)$$

The numerical values of this function which are given in Table 2 refer to an energy of 21,000 calories per gram-mole at 300° K. They illustrate clearly how much greater is the fraction of active molecules according to the generalized Boltzmann law than according to the familiar law, and what error is introduced by using the approximate formula (57) instead of the accurate expression (53).

If the velocity of chemical reaction is simply proportional to the fraction of the total number of molecules possessing an energy of activation,  $E$ , distributed in this way, then  $E$  must, according to equation (11), be related as follows to the apparent energy of activation:

$$E_A = E - FRT. \quad (58)$$

Table 2

*The Fractional Numbers of Molecules possessing an Energy of 21,000 Calories per Gram-mole at a Temperature of 300° K., for Various Numbers, F, of Internal Degrees of Freedom*

F	$\frac{dN}{N} = e^{-E/RT} \left( \frac{E}{RT} \right)^F \frac{1}{F!}$
0	$6.3 \times 10^{-16}$
1	$221 \times 10^{-16}$
2	$3,864 \times 10^{-16}$
3	$45,080 \times 10^{-16}$
4	$394,500 \times 10^{-16}$
5	$2,761,000 \times 10^{-16}$
6	$16,100,000 \times 10^{-16}$

This equation has the same form as equation (13), which follows from Trautz's treatment, and is identical with it if we substitute  $F = -C/R$ .

The method of applying this theory to reactions in the gaseous state consists of a comparison of the observed rate of reaction (actually,  $k_2$ , of equation (42)) with that computed by means of the equation

$$k_2 = (r_A + r_B)^2 \left( \frac{8\pi kT}{\mu} \right)^{\frac{1}{2}} \frac{(E/RT)^F}{F!} e^{-E/RT}. \quad (59)$$

When only one internal degree of freedom is concerned, we have

$$k_2 = (r_A + r_B)^2 \left( \frac{8\pi kT}{\mu} \right)^{\frac{1}{2}} \left( 1 + \frac{E}{RT} \right) e^{-E/RT}. \quad (60)$$

If no internal degrees of freedom come into play, we recover equation (35). Trial and error then lead to values of  $F$  which are, possibly excepting nitrogen pentoxide, reasonable ones.

In applying the theory to reactions in solution, the method depending on the magnitude of the absolute rate in regions of low molecular concentrations is clearly not applicable, and other methods must be devised. The first of these is based on the supposition that two comparable chemical changes can be regarded as invoking the same number of internal degrees of freedom. When two structurally comparable molecules undergo the same type of change in the same environment, it is not unreasonable to suppose that the frequency of collisions also is the same for the two. If the theory of an activation energy shared among a number,  $F$ , of internal degrees of freedom holds, we then have, for the ratio of the rates of the two reactions,

$$\frac{k_1}{k_2} = e^{-(E_1 - E_2)/RT} \left( \frac{E_1}{E_2} \right)^F \quad (61)$$

Some numerical values of  $F$  thus found† for the hydrolyses of glycosides, catalysed by hydrogen ion in aqueous solution, are reproduced in Table 3.

*Table 3*

*Estimates of the Number,  $F$ , of Internal Degrees of Freedom among which the Energy of Activation of Reactions in Solution may be shared*

Pairs of reactants	$F$
$\alpha$ -methylglucoside and $\beta$ -methylglucoside	45
Maltose and lactose	43
Melibiose and lactose	48
Maltose and trehalose	41
Fourteen different pairs	45

An interesting attempt, on different lines, to determine the value of  $F$  for reactions in solution was made by Ölander,‡ who, using a collision formula which is discussed in Chapter VIII, compared the rates of certain reactions in solution with those computed by an equation of the form of (59). In all but one of the reactions considered, the rate could be accounted for without appealing to the concept of internal activation. The exception was the inversion of cane sugar, for which  $F$  was estimated to be 4.

The two methods first used in applying the theory to solutions thus lead to values of  $F$  for the hydrolysis of sucrose which differ in order of magnitude. More recent experiments, to be discussed in the next chapter, have shown that the correct value, obtained by a third and more reliable method, is  $46 \pm 5$ . This number we may briefly pause to consider. A molecule containing  $n$  atoms is capable of  $3n$  modes of motion. Not all these modes, but possibly one-half of them, obey the classical dynamics upon which the considerations of this chapter are based. The number of atoms concerned in the activation of glycosides during their hydrolysis is thus about  $45/2$ , i.e. 30. We cannot say how this number is shared between the hydrated hydrogen ion plus neighbouring water molecules and the glycoside molecule itself. Assuming a 50-50 basis, 5 molecules of the solvent and 5 groups of the pyranose ring may thus be involved. We can say of these figures, as it has been said of the somewhat smaller figures estimated in the decomposition of relatively simple molecules in the gas phase, that they are entirely reasonable ones.

† Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 81, 503, (1929).

‡ *Z. physikal. Chem.*, **A**, **144**, 118, (1929).

All good theories do more than is initially expected of them; and the present one is no exception. Developed to account for a sufficient rate of production of activated molecules in the gaseous state, it has proved helpful in understanding catalysis in solution. The extent to which a solvent enters into partnership with a solute molecule is reflected in the number of degrees of freedom which are at work, and, to extend Fischer's lock-and-key metaphor, *F* for enzyme reactions may give us some idea of the size of the key.

## II

### THE VARIATION OF REACTION VELOCITY WITH RESPECT TO TEMPERATURE

ACCORDING to the general theory of activation, the rate at which molecules undergo chemical transformation is proportional to the number of molecules in an appropriately activated condition. This number, in turn, is an exponential function of the temperature and of the energy of activation, and usually determines the order of magnitude of the reaction velocity. The satisfactory investigation of the kinetics of any chemical change must consequently include as accurate an evaluation of the critical increment as experiment will permit. As we have seen, the variation with temperature of the velocity constant for a thermal reaction occurring in solution may often be expressed in the approximate form

$$k = Ae^{-E_A/RT}$$

or

$$\ln k = \ln A - \frac{E_A}{RT}. \quad \text{I (4)}$$

The constants  $A$  and  $E_A$ , which are specific for each reaction, may thus be determined by plotting  $\ln k$  against  $1/T$ ; the slope of the curve is  $-E_A/R$ , and the intercept on the  $\ln k$  axis is  $\ln A$  (Fig. 1). In practice, it is more convenient to obtain the value of  $E_A$  only from the graph, when  $A$  can be found by inserting into the equation the values of  $k$  and  $T$  corresponding to any point on the curve. When velocity constants at only two temperatures are concerned,  $E_A$  may be calculated from the expression

$$E_A = \frac{RT_2 T_1 \ln \frac{k_2}{k_1}}{T_2 - T_1} \quad \text{(1)}$$

The precision with which the quantities  $E_A$  and  $A$  can be determined clearly depends on the range of temperature within which measurements are possible, on the sensitiveness of the temperature control, as well as on the numerical accuracy assignable to the velocity constants.

#### *Methods of Measuring the Velocity of Reaction*

The most usual procedure for following the course of a chemical reaction entails the removal of samples of the reaction mixture, and the arrest of chemical change either by quickly cooling or by running

into a suitable chilling preparation. The composition of the system from time to time can then be determined by the ordinary methods of analysis. Reactions involving a change in the concentration of acids, bases, halides, and so forth may conveniently be followed by titrations. Organic groups also may be estimated by the usual

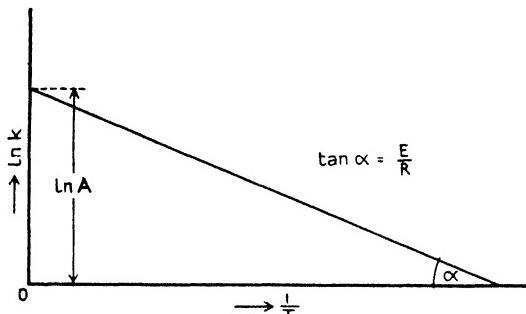


FIG. 1.

means.<sup>†</sup> It is advantageous, wherever possible, to use two independent methods of estimation. For example, in the case of the union of triethylamine with ethyl iodide,



the rate may be measured by titrating samples against standard acid, to determine the amount of amine left, and against standard thiocyanate to determine the amount of iodide produced. The hydrolysis of sucrose has been studied by measuring the decrease in optical rotation and the increase in reducing power. Both methods give the same result. Were this not so, the existence of a side reaction would be indicated.

Reactions in solution which are attended by the formation of slightly soluble gases, such as nitrogen,<sup>‡</sup> oxygen,<sup>§</sup> carbon dioxide,<sup>||</sup> or carbon monoxide,<sup>††</sup> may be investigated manometrically.

Chemical change is usually associated with changes in physical properties, any one of which is available for measuring the rate of reaction, provided blank experiments have revealed the desired

<sup>†</sup> e.g. amino nitrogen by the van Slyke method.

<sup>‡</sup> e.g. from diazoacetic ester (Bredig and Fraenkel, *Z. physikal. Chem.*, **60**, 207, (1907)), nitrosotriacetanamine (Goodall and Lewis, *ibid.*, **137**, 45, (1928)), and diazonium salts (Cain and Nicoll, *Trans. Chem. Soc.*, **81**, 1412, (1902)).

<sup>§</sup> e.g. from hydrogen peroxide (Harned, *J. Amer. Chem. Soc.*, **40**, 1461, (1918)).

<sup>||</sup> e.g. from acetonedicarboxylic acid (Wiig, *J. Physical Chem.*, **32**, 961, (1928)).

<sup>††</sup> e.g. from formic acid (Meyer, *Z. Elektrochem.*, **15**, 506, (1909)).

proportionality between amount of chemical substance and extent of physical property. Some of the properties of solutions which have been utilized kinetically are: colour,<sup>†</sup> viscosity,<sup>‡</sup> specific volume,<sup>§</sup> optical rotation,<sup>||</sup> electrical conductivity,<sup>††</sup> refractive index,<sup>††</sup> freezing-point,<sup>§§</sup> coagulation power,<sup>|||</sup> extinction coefficient,<sup>†††</sup> and phase boundary potential.<sup>†††</sup>

The selection of the most suitable method depends upon the nature of the reaction and upon other circumstances. Preference should be given to a method which allows the same reaction system to be examined continuously, without the removal of samples. With the polarimetric, dilatometric, manometric, and spectroscopic techniques, for example, the same volume of reaction mixture is kept in a vessel from start to finish, suitably jacketed by thermostat liquid or vapour.

For measuring the velocity of reactions which are too rapid to be followed by ordinary chemical or physical methods of analysis, Hartridge and Roughton<sup>§§§</sup> have devised a streaming method, which makes possible the accurate determination of velocity coefficients for reactions with a half-life of one-thousandth part of a second. The

<sup>†</sup> The addition of hydrocyanic acid to camphorquinone (Lapworth, *Trans. Chem. Soc.*, **83**, 995, (1903)); the reduction of ferric chloride by stannous chloride (Harcourt, *Phil. Trans.*, A, **212**, 187, (1913)); the conversion of creatine into creatinine (Edgar and Wakefield, *J. Amer. Chem. Soc.*, **45**, 2242, (1923)).

<sup>‡</sup> Numerous reactions studied by Schroeder (*Z. physikal. Chem.*, **45**, 75, (1903)) and by Dunston and Mussell (*Trans. Chem. Soc.*, **99**, 565, (1911)); the hydrolyses of esters in heavy water (Hornel and Butler, *ibid.*, 1361, (1936)).

<sup>§</sup> Decomposition of diacetone alcohol (Koelichen, *Z. physikal. Chem.*, **33**, 129, (1900)); hydrolysis of dimethyl acetal (Brönsted and Grove, *J. Amer. Chem. Soc.*, **52**, 1394, (1930)).

<sup>||</sup> Mutarotation of optically active substances; hydrolysis of disaccharides, trisaccharides, and glycosides generally. For the modern improvements in polarimetric methods, see Lowry, *Optical Rotatory Power*, Longmans, (1936).

<sup>††</sup> Electrical conductivity determinations are described by C. W. Davies, *The Conductivity of Solutions*, 2nd ed., Chapman and Hall, (1933). See also S. H. Maron and V. K. La Mer, *J. Amer. Chem. Soc.*, **61**, 692, (1939); H. and L. P. T. de Puente, *An. Asoc. Quim. Arg.* **33**, 171, (1945).

<sup>††</sup> Hydrolysis of sucrose (Duane, *Am. J. Sci.*, **11**, 349, (1901)). The measurement of the dielectric constant should nowadays prove helpful, since this can be made with great accuracy.

<sup>§§</sup> Isomerization of phenylbenziminophenyl ether in the fused state (A. W. Chapman, *Trans. Chem. Soc.*, **127**, 1992, (1925)).

<sup>|||</sup> Conversion of cis dichlorodiyethylenediaminochromchloride into an aquo-derivative (Freundlich and Pape, *Z. physikal. Chem.*, **86**, 458, (1914)).

<sup>†††</sup> The reaction between iodine and ethyl alcohol (Batley, *Trans. Faraday Soc.*, **24**, 438, (1928)). The hydration of acetic, propionic, and the mixed anhydride in aqueous solution (Barr and Plyler, *J. Chemical Physics*, **4**, 90, (1936)).

<sup>†††</sup> The saponification of stearolactone (Schulman and Rideal, *Proc. Roy. Soc.*, A, **130**, 259, (1930)); Fosbinder and Rideal, *ibid.*, **143**, 61, (1933)).

<sup>§§§</sup> *Ibid.*, A, **104**, 376, (1923).

principle is a simple one. Reactants are mixed in a compartment, from which they are made to flow rapidly down a capillary tube, at various points of which the fluid is examined by optical, thermal, or electrical means. If the streaming velocity is  $v$ , and the distance of the mixer from the point of observation is  $d$ , the time during which reaction has been proceeding is  $d/v$ . Simultaneous recording of observations at different positions down the tube supplies an instantaneous picture of the course of reaction. The Hartridge-Roughton method, although evolved for the examination of biochemical systems,<sup>†</sup> has already been applied, by von Halban and Eisner,<sup>‡</sup> to some of the reactions of inorganic chemistry.

Certain chemical changes, such as those responsible for the luminosity of insects, are attended by the evolution of light, and, though rapid, can be accurately studied cinematographically.<sup>§</sup>

### *Unimolecular Reactions*

A reaction is said to be unimolecular when the number of molecules decomposing at any instant is proportional to the total number of molecules present at that instant. If  $a$  is the initial concentration of the reactant, and  $x$  the amount which has been transformed in time  $t$ , then

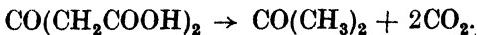
$$\frac{dx}{dt} = k_1(a-x).$$

$k_1$  thus denotes the constant fractional number of molecules which undergo chemical change in an infinitesimally short time interval. Integration gives

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x}. \quad (2)$$

The unimolecular constant has therefore the dimensions of a frequency, and an absolute value which is independent of the unit in which the concentration is expressed.

Acetonedicarboxylic acid decomposes unimolecularly in aqueous solution, with the elimination of carbon dioxide:



By titrating the amount of acid remaining at various time intervals, after removing the carbon dioxide in a stream of nitrogen, Wiig<sup>||</sup>

<sup>†</sup> See Hartridge, Millikan, and Roughton, *ibid.*, B, 116, 185, (1934).

<sup>‡</sup> *Helv. Chim. Acta*, 18, 724, (1935); *ibid.*, 19, 915, (1936).

<sup>§</sup> Harvey, *Ergebnisse der Enzymforschung*, 4, 365, (1935).

<sup>||</sup> *J. Physical Chem.*, 34, 596, (1930).

determined the velocity constants given in Table 1. The Arrhenius equation takes the form  $\ln k_1 = 32.26 - 23200/RT$  (Fig. 2). The results for the same reaction, studied by the manometric method,<sup>†</sup> give  $\ln k_1 = 32.00 - 23350/RT$ . The previous value of the critical

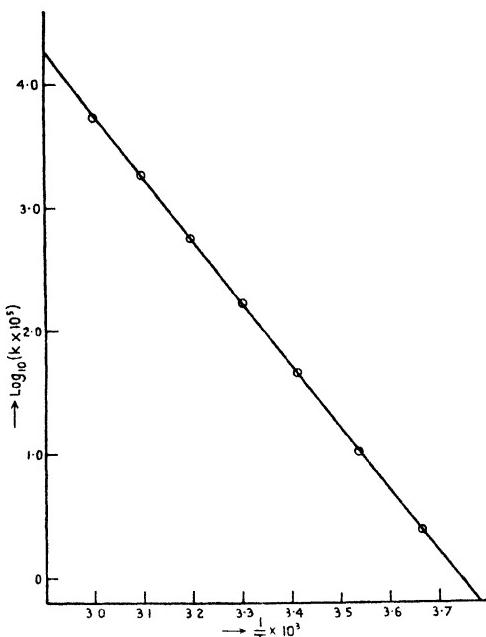


FIG. 2. Decomposition of acetonedicarboxylic acid in aqueous solution.  
Unimolecular.  $E_A = 23,200$  calories.

increment given by Wimark<sup>‡</sup> is 23,090 calories. Thus independent observations by two investigators, using different methods, yield a

*Table 1*  
*Decomposition of Acetonedicarboxylic Acid in Aqueous Solution*

$t^\circ \text{ C.}$	$k_1 \times 10^5 (\text{seconds}^{-1})$	
	Observed	By the Arrhenius equation
0	2.46	2.41
10	10.8	10.8
20	47.5	44.9
30	163	167
40	576	565
50	1,850	1,830
60	5,480	5,400

<sup>†</sup> Wiig, *J. Physical Chem.*, **32**, 961, (1928). <sup>‡</sup> *Acta medica Scand.*, **53**, 393, (1920).

value of  $E_A$  which is reproducible to within  $\pm 150$  calories of the mean of all sets of observations.

The rate of this reaction is uninfluenced by changing the material of the vessel in which the reaction is carried out, so that the decomposition proceeds entirely in the homogeneous liquid phase. This is generally, although not always, true of reactions which are measured in solution; the ease with which velocity constants can be reproduced without discriminating between reaction vessels of different material and dimensions indicates the absence of any heterogeneous decomposition on the walls, and renders it unnecessary to carry out special experiments in this direction. The hydrolysis of sucrose, however, and a few other reactions have been investigated in vessels packed with glass beads, but the increased surface thus afforded does not influence the rate of inversion.<sup>†</sup> The decomposition of hydrogen peroxide, on the other hand, in aqueous and in alkaline solution, is definitely influenced by the walls of the reaction vessel, the catalytic activity of glass being less than that of silica and greater than that of a wax-lined surface. In quartz vessels the reaction is apparently homogeneous.<sup>‡</sup> Traces of dust catalyse the reaction.<sup>§</sup> Instances of this kind of behaviour are rather exceptional. A solute molecule does not usually increase its chances of decomposing by leaving the bulk of the solution to take up a position on the wall. Certain reactions are known which proceed in solution by a chain mechanism; the discovery that such reactions show a pronounced wall effect would not be surprising.

### Bimolecular Reactions

The velocity with which methyl iodide and sodium ethoxide react in ethyl-alcoholic solution is proportional to the concentration of each of the two reactants:



Starting with concentrations of  $a$  and  $b$  respectively, the rate after time  $t$ , when  $x$  gram molecules of products have been formed per litre, is

$$\frac{dx}{dt} = k_2(a-x)(b-x)$$

or

$$k_2 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}. \quad (3)$$

<sup>†</sup> Speranski, *Z. physikal. Chem.*, **5**, 607, (1890).

<sup>‡</sup> A. C. Robertson, *J. Amer. Chem. Soc.*, **53**, 382, (1931).

<sup>§</sup> Pana, *Trans. Faraday Soc.*, **24**, 486, (1928).

By titration methods, Hecht and Conrad† found the following values for the bimolecular constant at various temperatures. They are seen to be in good agreement with the equation  $\ln k_2 = 26.21 - 19490/RT$  (Fig. 3).

*Table 2*  
*Formation of Methylmethylether in Ethyl-alcoholic Solution*

$t^\circ \text{ C.}$	$k_2 \times 10^8$ (litres/gram molecule second)	
	Observed	By the Arrhenius equation
0	5.60	5.50
6	11.8	11.9
12	24.5	24.5
18	48.8	50.1
24	100	100
30	208	193

If the initial concentrations of the two types of molecules participating in a bimolecular reaction are equal, we have

$$\frac{dx}{dt} = k_2(a-x)^2,$$

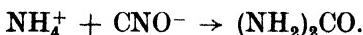
which on being integrated gives

$$k_2 = \frac{1}{ta} \frac{x}{(a-x)}. \quad (4)$$

The rate at which ammonium cyanate is converted into urea in aqueous solution is proportional to the square of the concentration of the salt:



As we shall see in Chapter IV, the velocity of reaction is governed by the number of activating collisions between the ammonium ion and the cyanate ion, the concentration of each of which is proportional to that of the salt:



The data of Walker and Hambly‡ conform closely with the equation

$$\ln k_2 = 29.08 - 23170/RT.$$

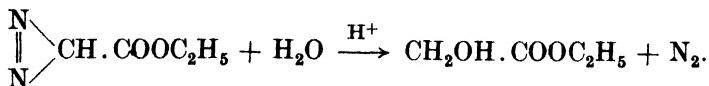
### *Catalysed Unimolecular Reactions*

A catalyst is a substance which, while undergoing no ultimate change in itself, is able to accelerate the rate at which other substances undergo chemical transformation. Diazoacetic ester is relatively stable in aqueous solution at ordinary temperatures. In the

† *Z. physikal. Chem.*, 3, 450, (1889).

‡ *Trans. Chem. Soc.*, 67, 746, (1895).

presence of very small concentrations of hydrogen ion, however, the ester decomposes rapidly:



By measuring the rate at which nitrogen was evolved from well-stirred solutions, Bredig and Fraenkel† found the velocity of reaction

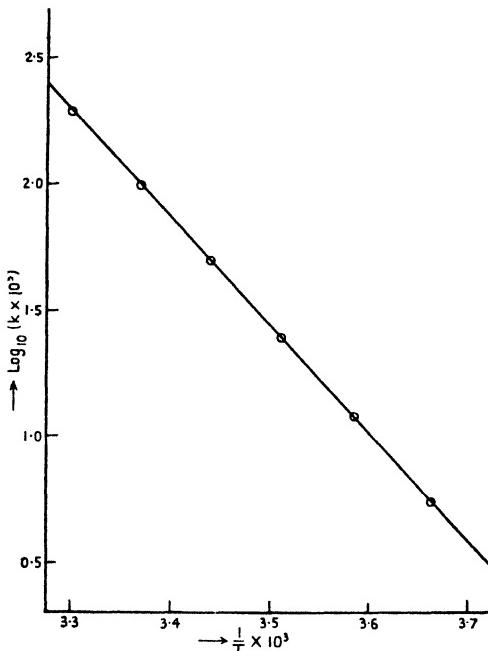


FIG. 3. Reaction between methyl iodide and sodium ethoxide in ethyl-alcoholic solution. Bimolecular.  $E = 19,490$  calories.

at any instant to be proportional to the concentration of ester present at that instant and to the (constant) concentration  $c_{\text{H}^+}$  of hydrogen ion; hence

$$\frac{dx}{dt} = k_2 c_{\text{H}^+} (a-x)$$

or

$$k_{\text{obs}} = k_2 c_{\text{H}^+} = \frac{1}{t} \ln \frac{a}{a-x}. \quad (5)$$

The reaction is thus essentially bimolecular, the rate depending on the number of encounters between hydrogen ions and ester molecules,

† *Z. Elektrochem.*, 11, 525, (1905).

although the data for any given concentration of catalyst conform to the unimolecular law. The value of  $k_2$ —sometimes referred to as the catalytic coefficient of the reaction—should thus be independent of the concentration of hydrogen ion and of the nature of the acid from which it is produced. Table 3 shows how adequately these conditions are fulfilled in dilute solutions.

The reaction is the classical instance of hydrogen ion catalysis, and is of service in estimating the concentration of hydrogen ion in systems where the commoner methods are not applicable.†

*Table 3*

*Decomposition of Diazoacetic Ester in Aqueous Acidic Solutions at 25° C.*

Catalysing acid	$c_{H^+} \times 10^4$ (gram ion/litre)	$k_{obs} \times 10^4$ (seconds <sup>-1</sup> )	$(k_2 = k_{obs}/c_{H^+}) \times 10^4$ (litres/gram mol. second)
Nitric	18.2	11.7	6.45
	9.09	5.77	6.33
Picric	9.09	5.93	6.53
	3.64	2.33	6.38
<i>m</i> -Nitrobenzoic	16.8	9.52	6.28
Fumaric	14.6	10.5	6.52
Succinic	7.24	4.75	6.42
Acetic	5.63	3.63	6.45

Fraenkel's data‡ are seen to accord well with the equation

$$\ln k_2 = 29.17 - 17480/RT.$$

*Table 4*

*Catalytic Decomposition of Diazoacetic Ester*

$t^\circ C.$	$(k_2 = k_{obs}/c_{H^+}) \times 10^4$ (litres/gram mol. second)	
	Observed	By the Arrhenius equation
15	2.28	2.33
25	6.42	6.41
35	16.9	16.5
45	41.4	41.4

### *Pseudo-unimolecular Reactions*

A bimolecular reaction of the type  $A + B \rightarrow$  Products, proceeding under such conditions that the concentration of  $A$  is greatly in excess

† The discovery that anions and undissociated molecules can catalyse reactions which had previously been considered to be sensitive to hydrogen ion only appeared to cast doubt for a time on the validity of this method. Fraenkel's work, however, has been confirmed by the subsequent failure to detect the catalytic influence of other ions towards this reaction (Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59, (1929)).

‡ *Z. physikal. Chem.*, **60**, 202, (1907).

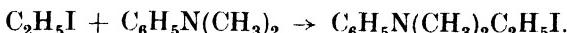
of that of  $B$ , will appear to be unimolecular. Reference to equation (3) shows that, since  $a \gg b$ , the maximum value of  $x$  is  $b$ , so that  $(a-x)$  can be regarded as approximately constant and equal to  $a$ ; hence

$$\frac{dx}{dt} = k_2 a(b-x)$$

and

$$k_{\text{obs}} = k_2 a = \frac{1}{t} \ln \frac{b}{(b-x)}. \quad (6)$$

The combination of ethyl iodide and dimethylaniline, when carried out at low concentrations in an inert solvent, is bimolecular:



If dimethylaniline be used as a solvent, the reaction is unimolecular

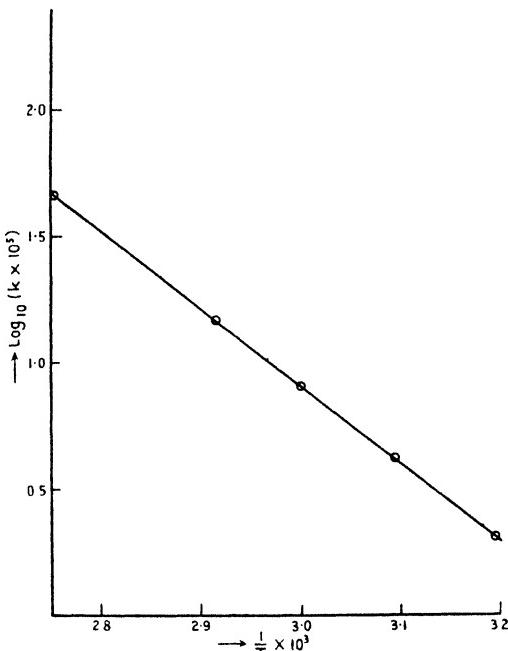


FIG. 4. Combination of ethyl iodide with dimethylaniline, in dimethylaniline as solvent. Pseudo-unimolecular.  $E = 14,000$  calories.

with respect to the iodide. Hirniak's data† for the reaction under these conditions agree with the equation  $\ln k_{\text{obs}} = 11.79 - 14000/RT$  (Fig. 4).

Had ethyl iodide been used as a solvent, the reaction would have

† *Tables Annuelles*, 2, 508, (1911).

been unimolecular with respect to the other reactant: the change must thus be of the second order. This is one of the various methods, to be discussed later, for determining the order of reaction.

Table 5

*Unimolecular Constants for the Combination of Ethyl Iodide with Dimethylaniline in Dimethylaniline as Solvent*

$t^{\circ}$ C.	$k_{\text{obs}} \times 10^8$ (seconds $^{-1}$ )	
	Observed	By the Arrhenius equation
40	2.05	2.04
50	4.09	4.12
60	7.93	7.94
70	14.7	14.7
90	46.0	45.9

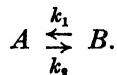
The hydration of acetic anhydride is bimolecular in acetone and in acetic acid solutions,<sup>†</sup> but is unimolecular with respect to the anhydride in aqueous solution:<sup>‡</sup>



The hydration of acid anhydrides in water and their esterification in alcoholic solution, as well as uncatalysed hydrolyses in aqueous solution, belong to the class of pseudo-unimolecular changes.

### *Opposing Unimolecular Reactions*

When a chemical change proceeds not to completion but to an equilibrium stage, it becomes necessary to allow for this fact in deriving the kinetic equations. Relations of greater complexity result, their form depending on the order of the direct and reverse reactions. We shall deal here with the simplest case, i.e. when both changes are unimolecular. Let the initial concentrations of *A* and *B* be *a* and *b* respectively; and let their concentrations at time *t* be  $(a-x)$  and  $(b+x)$ .



$$(a-x) \quad (b+x).$$

Then 
$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_1(a-x) - k_2(b+x),$$

<sup>†</sup> Philip, *Trans. Chem. Soc.*, **28**, 259, (1912).

<sup>‡</sup> Rivett and Sidgwick, *ibid.*, **97**, 732, (1910); Orton and Jones, *ibid.*, **101**, 1708, (1912).

which gives on integration

$$k = (k_1 + k_2) = \frac{1}{t} \ln \frac{S}{S-x}, \quad (7)$$

where

$$S = \frac{k_1 a - k_2 b}{k_1 + k_2}.$$

When equilibrium has been reached,

$$\frac{dx}{dt} = 0;$$

hence

$$k_1(a-x) = k_2(b+x).$$

The ratio

$$\frac{k_1}{k_2} = \frac{b+x}{a-x}$$

is termed the equilibrium constant, and is denoted by  $K$  (Chapter VI). If the initial reaction mixture contains only one reactant ( $b = 0$ ),

$$S = \frac{a}{1+k_2/k_1} = \frac{a}{(1+K)}.$$

The interconversion of  $\gamma$ -hydroxybutyric acid and its lactone† and of  $d$ - and  $l$ -menthone‡ conform with this equation. So also does the mutarotation of glucose, and certain other sugars, which must be referred to in some detail.

$\alpha$ -Glucose, which has a specific optical rotation of  $+110.0^\circ$ , when dissolved in water is converted into a mixture which has a stable rotation of  $+52.56^\circ$ . Similarly,  $\beta$ -glucose, with an initial rotatory power of  $+19.7^\circ$ , is converted into the same mixture. Lowry§ explained these changes in terms of dynamic isomerism, the final mixture in each case representing equilibrium amounts of  $\alpha$ - and  $\beta$ -glucose, with possibly a minute quantity of an intermediate form. The changes are accelerated by acids, and to a much greater extent by bases. The temperature coefficient of the velocity of mutarotation of glucose in water was investigated by Hudson and Dale,|| who, supplementing their results with those of Lowry (*loc. cit.*), Trey,†† Osaka,†† and others, have compiled the following table. As is to be expected, the observed velocity ( $k_\alpha + k_\beta$ ), whether we examine pure  $\alpha$ - or  $\beta$ -glucose, has the same value. Independent experiments show

† Henry, *Z. physikal. Chem.*, **10**, 98, (1892).

‡ Vorländer, *Berichte*, **36**, 268, (1903).

§ *Trans. Chem. Soc.*, **75**, 212, (1899).

|| *J. Amer. Chem. Soc.*, **39**, 320, (1917).

†† *Z. physikal. Chem.*, **18**, 193, (1895).

†† *Ibid.*, **35**, 661, (1900).

Table 6

$t^\circ\text{ C.}$	$(k_\alpha + k_\beta) \times 10^4$ (minutes $^{-1}$ ; $\log_{10}$ )		
	$\alpha$ -glucose	$\beta$ -glucose	By the Arrhenius equation
0·7	7·4	7·4	7·4
5	12·9	15·0	12·2
10	23·5	22·3	21·6
15	39·9	37·9	37·4
20	63·5	65·4	63·3
25	105	106	106
30	175	168	173
40	437	395	442

the equilibrium constant  $K \left( = \frac{[\beta\text{-glucose}]}{[\alpha\text{-glucose}]} = \frac{k_\alpha}{k_\beta} \right)$  to have a value of 0·575 which is unaffected by temperature, hence the heat of reaction is zero, and over the complete temperature range

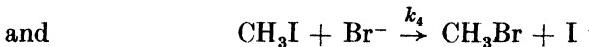
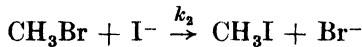
$$k_\alpha = k \times \frac{1\cdot739}{2\cdot739} \quad \text{and} \quad k_\beta = k \times \frac{1}{1\cdot739}.$$

The Arrhenius equation, in the units referred to, takes the form  $\log_{10}(k_\alpha + k_\beta) = 11\cdot0198 - 3873/T$ . Converting the constants into the customary units, we have

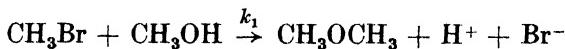
$$\ln(k_\alpha + k_\beta) = 22\cdot12 - \frac{17700}{RT}.$$

### *Opposing Bimolecular Reactions*

Let us consider the two fairly simple opposing reactions



in methylalcoholic solution. Like the corresponding changes in water they are not entirely free from complications, but are attended by some slight reaction with the solvent, according to the equations



Conditions can, however, be so chosen that the exchange is virtually complete, while only subanalytic amounts of the organic halide have reacted with the solvent. The order of both exchange reactions is the second, as is established by a tenfold variation in the concentration.

For systems with equal concentrations of methyl bromide and potassium iodide, we have†

$$k_2 = \frac{\sqrt{K}}{2ta} \ln \left\{ \frac{a-x(1-1/\sqrt{K})}{a-x(1+1/\sqrt{K})} \right\}, \quad (8)$$

where

$$a = [\text{CH}_3\text{Br}]_0 = [\text{I}^-]_0,$$

$$x = [\text{CH}_3\text{I}]_t = [\text{Br}^-]_t,$$

and

$$K = \frac{[\text{Br}^-]_\infty [\text{CH}_3\text{I}]_\infty}{[\text{I}^-]_\infty [\text{CH}_3\text{Br}]_\infty}.$$

For systems with unequal concentrations of reactants, we have the following expression for the bimolecular velocity coefficient of the reverse reaction:

$$k_4 = \frac{1}{2t(K-1)D} \ln \left\{ \frac{1 + \frac{y}{C+D}}{1 + \frac{y}{C-D}} \right\}, \quad (9)$$

where

$$C = (c+d)/2(K-1),$$

$$D = \{(c-d)^2 + 4Kcd\}^{1/2}/2(K-1),$$

$$c = [\text{CH}_3\text{I}]_0,$$

$$d = [\text{Br}^-]_0,$$

and

$$y = [\text{CH}_3\text{Br}]_t = [\text{I}^-]_t.$$

Table 7 gives the experimental results‡ and those calculated by means of the equations

$$k_2 = 2.26 \times 10^{10} \times e^{-18250/RT}$$

and

$$k_4 = 3.91 \times 10^{11} \times e^{-21400/RT}.$$

The estimated uncertainties in the critical increments are  $\pm 250$  and  $\pm 1,000$  calories respectively.

*Table 7*  
*Bimolecular Constants for the Opposing Reactions*  
 $\text{CH}_3\text{Br} + \text{I}^- \rightleftharpoons \text{CH}_3\text{I} + \text{Br}^- \text{ in } \text{CH}_3\text{OH}$

$T^\circ$	$k_2 \times 10^4$ (litres/mole second)		$T^\circ$	$k_4 \times 10^5$ (litres/mole second)	
	Observed	By the Arrhenius equation		Observed	By the Arrhenius equation
273.1	c. 0.52	0.568	273.1	0.294	0.297
288.58	3.53	3.50	293.51	4.54	4.59
297.58	9.34	9.21	303.27	13.8	14.9
307.68	2.43	2.48	313.36	45.4	47.0
317.73	6.35	6.37	322.23	121	121

† Bodenstein, *Z. physikal. Chem.*, **29**, 295, (1898).

‡ Moelwyn-Hughes, *Trans. Faraday Soc.*, **35**, 368, (1939).

### Consecutive Unimolecular Reactions

Chemical change sometimes takes place in stages, each of which is characterized by a separate velocity coefficient, as, for example, when a reactant,  $A$ , is converted unimolecularly into a compound,  $M$ , which is further converted unimolecularly into the product,  $B$ .



If  $a$  is the initial concentration of the reactant, and  $x$ ,  $y$ , and  $z$  are the concentrations, at time  $t$ , of the reactant, the intermediate compound, and the product, respectively, we have the following differential equations:

$$-\frac{dx}{dt} = k_1 x,$$

$$+\frac{dz}{dt} = k_2 y,$$

and

$$+\frac{dy}{dt} = k_1 x - k_2 y,$$

which yield, on integration,

$$(x+y) = (a-z) = a \left\{ \frac{k_1}{k_1 - k_2} e^{-k_1 t} - \frac{k_2}{k_1 - k_2} e^{-k_2 t} \right\}. \quad (10)$$

The velocities of oxidation of oxalic acid by aqueous acidic potassium permanganate,<sup>†</sup> of the mutarotation of  $\alpha$ - and  $\beta$ -galactose in water,<sup>‡</sup> and of the mutarotation of aluminium benzoylcamphor in carbon tetrachloride solution<sup>§</sup> are expressible by an equation of this form.

The intermediate compound, it will be observed, is formed by one process and destroyed by another, hence its concentration depends on the relative magnitudes of  $k_1$  and  $k_2$ . When  $k_2 \gg k_1$ ,  $y$  is small, and the total rate of reaction is almost that of the first step,  $A \rightarrow M$ , which is given by  $x = ae^{-k_1 t}$ . When  $k_2 \ll k_1$ ,  $z$  is small, and the net rate is nearly that of the second step,  $M \rightarrow B$ , which is given by  $y = ae^{-k_2 t}$ . Unless  $k_1$  and  $k_2$  are commensurate, therefore, the velocity reduces to that of the slower of the two unimolecular processes. The net observed velocity in a sequence of changes is the velocity of the slowest process. This is a general and widely used principle of chemical kinetics.

<sup>†</sup> Harcourt and Esson, *Phil. Trans.*, **156**, 193, (1866).

<sup>‡</sup> G. F. Smith and Lowry, *Trans. Chem. Soc.*, 666, (1928).

<sup>§</sup> Lowry and Traill, *Proc. Roy. Soc., A*, **132**, 416, (1931).

The most frequent application of equation (10) has been to the hydrolysis of esters of dibasic acids, for which, provided each cleavage is unimolecular, we find the following law for the dependence of the hydrogen ion concentration on time:

$$\frac{[\text{H}^+]_{\infty} - [\text{H}^+]_t}{[\text{H}^+]_0} = \frac{2k_2 - k_1}{k_2 - k_1} e^{-k_1 t} - \frac{k_1}{k_2 - k_1} e^{-k_2 t}. \quad (11)$$

### *Autocatalysed Reactions*

A chemical change which is hastened by one of its own products is said to be autocatalysed. The interaction between acetone and bromine in aqueous acidic solution affords an interesting example. Apart from the autocatalytic effect, the change proceeds by way of a fascinating mechanism which was elucidated by Lapworth.<sup>†</sup> For our present purpose it will be expedient to consider first the reaction between acetone and iodine, which has been shown to have precisely the same mechanism.<sup>‡</sup>

The net effect of the reaction between acetone and iodine in acidic solution is represented by the equation



The rate at which acetone disappears is found to be directly proportional to the concentrations of acetone and hydrogen ion but to be independent of the concentration of iodine. If we denote by  $a$  and  $c$  the initial concentrations of hydrogen ion and acetone respectively, and by  $x$  the amount of acetone which has been converted in time  $t$ , we have

$$\frac{-d[\text{CH}_3\text{COCH}_3]}{dt} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

or  $\frac{dx}{dt} = k(a-x)(c+x),$

which on integration gives

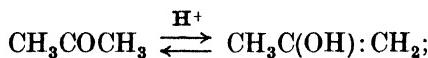
$$k = \frac{1}{t(a+c)} \ln \frac{a(c+x)}{b(a-x)}. \quad (12)$$

Lapworth's mechanism is consistent with all the facts known

<sup>†</sup> *Trans. Chem. Soc.*, **85**, 30, (1904).

<sup>‡</sup> Dawson, *ibid.*, **95**, 1860, (1909).

concerning the reaction. The measurable process consists of the enolization of acetone, the rate of which is proportional to  $[H^+]$ :



normally an equilibrium condition would be established between the keto and enol forms, but in the presence of iodine the following reaction sets in immediately and completely:



It is to be noted that, in spite of the slightly complicated nature of the reaction and the modified form which the expression for the velocity constant consequently assumes,  $k$  is simply a bimolecular coefficient denoting the rate at which acetone is enolized when its concentration and that of hydrogen ion are unity.

The influence of temperature on the value of  $k$  has been measured by Rice and Kilpatrick,<sup>†</sup> whose results are given in Table 8. On plotting  $\ln k$  against  $1/T$  in the usual way, we arrive at the expression  $\ln k = 24.41 - 20580/RT$ .

*Table 8*  
*The Enolization of Acetone in Aqueous Acidic Solution*

$t^\circ \text{ C.}$	$k \times 10^6$ (litres/gram molecule second)	
	Observed	By the Arrhenius equation
0	1.16	1.17
24	25.4	25.3
25	27.9	28.6
27	35.9	36.0
35	88.2	88.1

Rice, Fryling, and Wesolewski<sup>‡</sup> found the temperature coefficient for the velocity of this reaction to be independent of the nature of the catalysing acid and of the presence of a large number of electrolytes and non-electrolytes, although the actual velocity is affected. The average of 21 values for the ratio  $k_{25^\circ\text{C.}}/k_{23^\circ\text{C.}}$ , in close agreement with one another, is 1.2625; whence, by equation (1),  $E_A = 20350$  calories. Generally, the evaluation of  $E_A$  from velocities determined at two temperatures only—especially when these are in such close proximity—is inadmissible. In the present instance, however, there

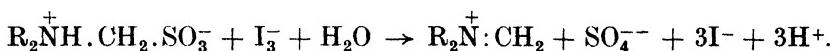
<sup>†</sup> *J. Amer. Chem. Soc.*, **45**, 1401, (1923).

<sup>‡</sup> *Ibid.*, **46**, 2405, (1924).

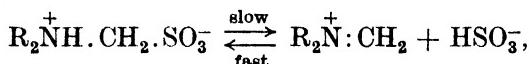
is fair agreement between the two values quoted although greater reliance is to be placed on the former result.

The reaction of aldehydes with bromine and iodine follows the same course,<sup>†</sup> though a certain amount of oxidation occurs at the same time, especially with bromine. Strong evidence in favour of the view that the velocity actually measured is that of enolization is afforded by the identity in the velocity constants found for the two halogens.

Certain similar features are borne by a number of reactions which have been investigated by T. D. Stewart and W. E. Bradley.<sup>‡</sup> Although the changes do not exhibit autocatalysis, they may conveniently be discussed at this stage. Disubstituted aminomethyl-sulphonic acids react in aqueous solution with three oxidizing agents—iodine, bromine, and hydrogen peroxide—at exactly the same rate:



The velocity, moreover, is unimolecular with respect to the acid and independent of the concentration of the oxidizing agent, even when this is present in minute amounts. The authors point out that these facts indicate the measurable process to be the slow attainment of the equilibrium



which is followed by the rapid oxidation



It may be mentioned that this last reaction, although rapid in comparison with the rate-determining step, has probably a measurable velocity, just like the oxidation of arsenite (p. 94) and sulphite ions (p. 333).

### *Termolecular Reactions*

Let us consider a reaction wherein three molecules undergo simultaneous chemical change,  $A+B+C \rightarrow \text{Products}$ . Employing the usual notation, we have

$$\frac{dx}{dt} = k_3(a-x)(b-x)(c-x)$$

<sup>†</sup> Dawson, Burton, and Ark, *Trans. Chem. Soc.*, 1275, (1914).

<sup>‡</sup> *J. Amer. Chem. Soc.*, 54, 4183, (1932).

$$\text{or } k_3 = \frac{1}{t} \left\{ \frac{1}{(a-b)(c-a)} \ln \frac{a}{a-x} + \frac{1}{(a-b)(b-c)} \ln \frac{b}{b-x} + \frac{1}{(b-c)(c-a)} \ln \frac{c}{c-x} \right\}. \quad (13)$$

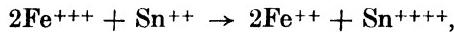
When the three reactants are present at a common concentration ( $a = b = c$ ), there result the simpler expressions

$$\frac{dx}{dt} = k_3(a-x)^3$$

and

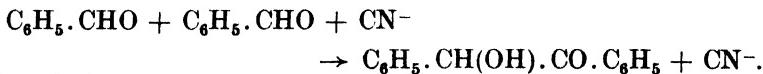
$$k_3 = \frac{1}{2t} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\}. \quad (14)$$

These equations have long been considered adequate† for a kinetic description of the reactions



Given experiments under stipulated conditions may certainly be described by means of these simple expressions, but when the reactions are studied under a wide variety of conditions, it becomes clear that the reactions are more complicated than these equations imply.‡

The least complicated termolecular reaction hitherto examined in solution is the polymerization of benzaldehyde under the influence of the cyanide ion in water:



The relation

$$\frac{d[\text{Aldehyde}]}{dt} = k_3[\text{Aldehyde}]^2[\text{Cyanide}]$$

has been found to hold accurately over a wide range of conditions by Stern,§ some of whose results are reproduced in Table 9. The data may be summarized in the form

$$k_3 = 7.20 \times 10^5 e^{-13220/R T},$$

the termolecular constants being in (litres/gram molecule)<sup>2</sup> per second.

† Noyes, *Z. physikal. Chem.*, **16**, 546, (1895); Noyes and Cottle, *ibid.*, **27**, 578, (1898).

‡ For later work on the ferric-stannous reaction, see Timofeew, Muchin, and Gurewitsch, *ibid.*, **115**, 161, (1925); R. A. Robinson and Law, *Trans. Faraday Soc.*, **31**, 899, (1935).

§ *Z. physikal. Chem.*, **50**, 513, (1905); Bredig and Stern, *Z. Elektrochem.*, **10**, 582, (1904).

*Table 9*  
*Cyanide-ion Catalysis of the Benzoin Reaction*

$t^{\circ}$ C.	$k_s$ (secs. $^{-1}$ (moles/litre) $^2$ )	
	Observed	By the Arrhenius equation
25·0	$1\cdot40 \times 10^{-4}$	$1\cdot43 \times 10^{-4}$
40·0	$4\cdot33 \times 10^{-4}$	$4\cdot17 \times 10^{-4}$
49·9	$8\cdot00 \times 10^{-4}$	$8\cdot04 \times 10^{-4}$
60·0	$1\cdot48 \times 10^{-3}$	$1\cdot49 \times 10^{-3}$

Among other reactions which appear to be termolecular are the oxidation of ferrous sulphate in water,<sup>†</sup> the action of ammonia on ethyl malonate in ethyl-alcoholic solution,<sup>‡</sup> the reaction between iodide and ferric ions in water,<sup>§</sup> and that between benzoyl chloride and alcohols in etheric solutions.<sup>||</sup>

### *The Order of Chemical Reaction*

Many methods present themselves for determining the order of reaction but no hard and fast rule can be given for selecting the most suitable.

1. *The half-life method.* By substituting the value of  $\frac{1}{2}a$  for  $x$  in equations (2), (4), and (14), the times of half-completion for the various reactions are:

$$\text{Unimolecular} \quad t_{\frac{1}{2}} = \frac{\ln 2}{k_1}.$$

$$\text{Bimolecular} \quad t_{\frac{1}{2}} = \frac{1}{k_2 a}.$$

$$\text{Termolecular} \quad t_{\frac{1}{2}} = \frac{3}{2k_3 a^2}.$$

In general, for a reaction of the  $n$ th order,

$$t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}, \quad (15)$$

so that, if we measure the half-lives,  $t$  and  $t'$ , for initial concentrations of  $a$  and  $a'$  respectively, we have

$$n = 1 + \frac{\ln(t'/t)}{\ln(a/a')} \quad (16)$$

<sup>†</sup> Lamb and Elder, *J. Amer. Chem. Soc.*, **53**, 137, (1931).

<sup>‡</sup> Bailey, *Proc. Roy. Irish Acad.*, **B**, **39**, 567, (1930).

<sup>§</sup> Fräulein von Kiss, *Z. anorg. Chem.*, **198**, 102, (1931).

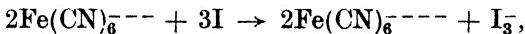
<sup>||</sup> Ashdown, *J. Amer. Chem. Soc.*, **52**, 268, (1930).

2. *The initial rate method.* For a reaction of the  $n$ th order, the initial velocity is  $v = dc/dt = kc^n$ . If  $v'$  is the corresponding expression when the initial concentration is  $c'$ , then

$$n = \frac{\ln\left(\frac{dc}{dt}\right)/\left(\frac{dc'}{dt}\right)}{\ln(c/c')}$$
 (17)

3. *The isolation method.* We have seen (p. 37) that the expression  $dx/dt = k_2(a-x)(b-x)$  for the rate of a bimolecular reaction reduces to one which is formally that for a unimolecular reaction ( $dx/dt = k_2 a(b-x)$ ) when one of the reactants is present in great excess. The rates of reactions of higher order may similarly be reduced;  $dx/dt = k_3(a-x)(b-x)(c-x)$  becomes  $dx/dt = k_3 ab(c-x)$  when both  $a$  and  $b$  are much greater than  $c$ . The true order of reaction is thus the sum of the separate apparent orders obtained by adjustment of the relative concentrations.

Variable kinetic orders have occasionally been reported,† especially for ionic reactions. The reason will become clear at a later stage. In the meantime, two methods may be mentioned for overcoming this difficulty. The apparent kinetic order may be plotted as a suitable function of the ionic concentration, and the value corresponding to  $c = 0$  be taken as the true order. The half-life method is applicable if the ionic strength is maintained constant while the concentration of ionic reactants is varied. Omission to adopt some such device probably accounts for high kinetic orders occasionally found in the earlier literature, e.g. the order of 5 ascribed by Donnan and le Rossignol‡ to the reaction



now replaced by the order of 3.§

A catalysed bimolecular reaction (p. 46) is essentially termolecular, just as a catalysed unimolecular reaction (p. 35) is essentially bimolecular. One function of a catalyst is thus to reduce the apparent order of reaction by unity.

The vast majority of chemical reactions which have been examined are bimolecular. The remaining ones are mostly of the first order. Termolecular reactions are few in number, and reactions of higher

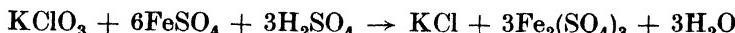
† e.g. van 't Hoff, *Studies in Chemical Dynamics*, p. 113, (1896).

‡ *Trans. Chem. Soc.*, **83**, 703, (1903).

§ Fräulein von Kiss, *Rec. trav. chim. Pays-bas*, **52**, 289, (1933).

order† extremely rare—a circumstance which is readily intelligible when the relative probabilities of the simultaneous encounter of two, three, or more molecules is considered.

The uncatalysed reactions hitherto discussed have a kinetic order agreeing with the chemical equation. Carboxylic acids are chemically capable of decomposing as single molecules, and are in fact found to do so. Methyl iodide, however, cannot yield dimethyl ether without the presence of a second molecule, such as methyl alcohol; and the reaction is bimolecular. Such agreement can obviously not be general. The reaction



is kinetically of the second order,‡ indicating that the net change consists of a sequence of many reactions, of which the slowest is bimolecular. Important theories have appeared in the numerous and varied attempts to reconcile stoichiometric complexity with kinetic simplicity.

### *Composite Reactions*

Chemical compounds not infrequently decompose by several different mechanisms, which, possessing separate velocity coefficients, are regarded as virtually independent. Thus the rate of mutarotation of glucose (which we shall denote by G) in aqueous solution may be expressed by the equation

$$-\frac{d[G]}{dt} = k_0[G] + k_{\text{H}^+}[\text{H}^+][G] + k_{\text{OH}^-}[\text{OH}^-][G]$$

or  $k = k_0 + k_{\text{H}^+}[\text{H}^+] + k_{\text{OH}^-}[\text{OH}^-]$ .

At 25° C., Hudson§ found the values

$$k_0 = 9.6 \times 10^{-3}, \quad k_{\text{H}^+} = 2.6 \times 10^{-1}, \quad k_{\text{OH}^-} = 9.8 \times 10^{+3},$$

in fairly close agreement with the later values of  $10.4 \times 10^{-3}$ ,  $3.3 \times 10^{-1}$ , and  $9.4 \times 10^{+3}$  given by Kuhn and Jacob.|| We have yet

† The inferred rate-determining step in the oxidation of hydrogen peroxide (Young and Bray, *J. Amer. Chem. Soc.*, **54**, 4284, (1932)) and of allyl alcohol (Schar and Riesch, *ibid.*, **58**, 667, (1936)) by aqueous bromate solutions is the quadrinolecular reaction  $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow$ .

‡ Hood, *Phil. Mag.*, **6**, 371, (1878); *ibid.*, **20**, 323, (1885).

§ *J. Amer. Chem. Soc.*, **29**, 1571, (1907).

|| *Z. physikal. Chem.*, **113**, 389, (1924). The units of  $k_0$  are minutes<sup>-1</sup>, and of  $k_{\text{H}^+}$  and  $k_{\text{OH}^-}$  litres per gram-molecule-minute, the logarithms being to the base 10. Hence, in order to convert them to seconds and natural logarithms, they must be multiplied by the factor 0.03838.

to discover whether the equation of Arrhenius is applicable to the separate velocity constants. Hudson and Dale (*loc. cit.*) found this to be the case, and, moreover, concluded that  $(E_A)_0$  and  $(E_A)_{H^+}$  had a common value of 17,700 calories, but later work (p. 308) has shown that  $(E_A)_0$  is slightly lower than  $(E_A)_{H^+}$ .

Greater differences are found between the various  $E_A$  values for other reactions. For example, the hydration of aqueous acetic anhydride gives us  $(E_A)_0 = 10,840$  and  $(E_A)_{H^+} = 17,280$  calories.† The decomposition of acetonedicarboxylic acid (p. 298) in the presence of aniline gives  $(E_A)_C = 13,900$  for the catalysed reaction. The Arrhenius energies of activation for the separate reactions may thus be greater or less than the composite value calculated from the relation

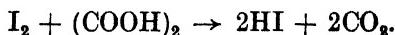
$$E_A = RT^2 \frac{d \ln k}{dT}, \quad I (11)$$

to which, of course, no physical meaning can now be attached.

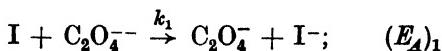
The hydrolysis of the  $\alpha$ -brompropionate ion in aqueous alkaline solution is typical of the rather numerous reactions which proceed by concurrent unimolecular and bimolecular mechanisms.‡

### *Less Simple Reactions*

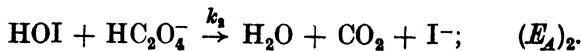
When iodine reacts with oxalic acid in aqueous solution, the following net change takes place:



The mechanism of the reaction may be resolved into at least two parts. One component of the total rate is independent of the concentration of hydrogen ions, and is proportional to the square root of the iodine concentration, indicating that the reaction



gives one rate-determining step; a second component of the total rate is adversely influenced by hydrogen ions, and is consistent with the occurrence of a second rate-determining step



† Rivett and Sidgwick, *loc. cit.*; Orton and Jones, *loc. cit.*; Verkade, *Rec. trav. chim. Pays-Bas*, 35, 79, 299, (1915); Jowett, *Thesis*, Liverpool, (1923).

‡ Senter, *Trans. Chem. Soc.*, 95, 1827, (1909).

These two processes are related to the two equilibria

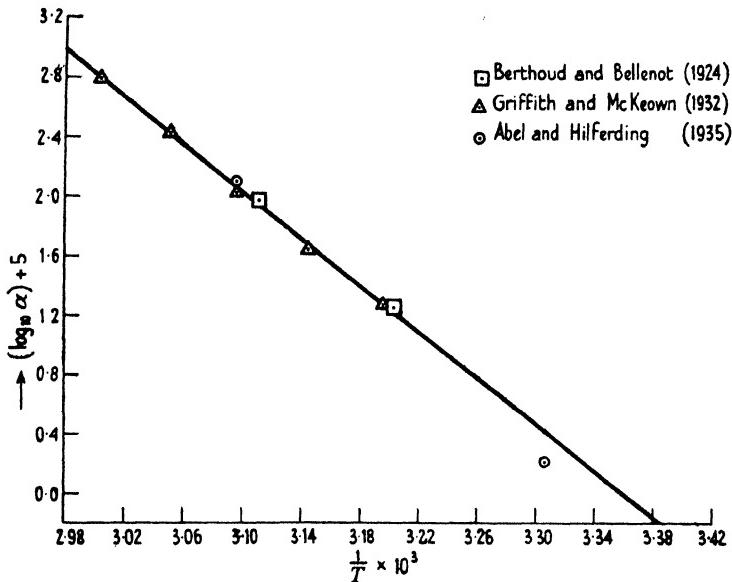
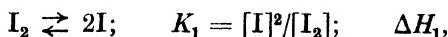


FIG. 5. The reaction between iodine atoms and monoxalate ions in aqueous solution.

both of which are considered to be established and maintained rapidly in comparison with the decomposition reactions. It follows that

$$\begin{aligned} -\frac{d[I_2]}{dt} &= k_1[C_2O_4^{2-}][I] + k_2[HC_2O_4^-][HIO] \\ &= \alpha[C_2O_4^{2-}][I_2]^{\frac{1}{2}} + \beta[HC_2O_4^-][I_2]/[H^+][I^-], \end{aligned}$$

where

$$\alpha = k_1 K_1^{\frac{1}{2}}$$

and

$$\beta = k_2 K_2.$$

Denoting by  $\Delta H_1$  and  $\Delta H_2$  the increase in total heat content associated with the dissociation and hydrolysis of iodine, it follows that

$$(E_A)_\alpha = (E_A)_1 + \frac{1}{2}\Delta H_1$$

and

$$(E_A)_\beta = (E_A)_2 + \Delta H_2.$$

In Fig. 5 we have plotted the experimentally determined values of  $\log_{10} \alpha$  against  $1/T$  in the usual way, combining the data of Berthoud

and Bellenot,<sup>†</sup> Griffith and McKeown,<sup>‡</sup> and Abel and Hilferding,<sup>§</sup>  $(E_A)_\alpha$  is found to be 36,100 calories. If the value of  $\Delta H_1$  found for the gaseous equilibrium (35,400 calories) is accepted,  $(E_A)_1$  becomes 18,400 calories. Similarly,  $(E_A)_2$  is found to be 16,590 calories.

Other halogens react with aqueous oxalic acid in a similar way, without, however, the complication of an atomic mechanism.<sup>||</sup>

### *Heterogeneous Reactions*

When a reaction occurs exclusively at the surface of a solid, the number of molecules decomposing per unit time is proportional to the number of adsorbed molecules. The amount ( $a$ ) of substrate adsorbed depends on the area ( $S$ ) of the surface and on the concentration ( $C$ ) of the substrate in the bulk of the solution. These quantities may sometimes be empirically related by the Freundlich isotherm,  $a = KSC^{1/n}$ , where  $n$  and  $K$  are constants. Whether the reaction considered is of the bimolecular kind, possessing a rate determined by the number of suitable impacts made by dissolved molecules upon the surface, or of a unimolecular type with a rate governed by the stability of the activated, adsorbed molecule, we have for the velocity of reaction

$$-\frac{dC}{dt} = k'C^{1/n},$$

which gives on integration

$$k' = \frac{1}{t} \frac{n}{n-1} \{C_0^{(n-1)/n} - C_t^{(n-1)/n}\}. \quad (18)$$

Sodium hypochlorite in aqueous solution at room temperatures is relatively stable, a slow decomposition of uncertain order setting in and reaching half completion in about three years. In the presence of small quantities of metallic oxides, however, a very rapid reaction takes place due to the catalytic decomposition of adsorbed hypochlorite ions:  $\text{ClO}^- \rightarrow \text{Cl}^- + \frac{1}{2}\text{O}_2$ . By measuring the volume of oxygen evolved, Chirnoaga<sup>††</sup> investigated the velocity of reaction under varying conditions. With nickel peroxide as catalyst,  $1/n$  is found to be 0.47. Values of  $k'$  determined at various temperatures using

<sup>†</sup> *Helv. Chim. Acta*, 7, 307, (1924).

<sup>‡</sup> *Trans. Faraday Soc.*, 28, 752, (1932).

<sup>§</sup> *Z. physikal. Chem.*, A, 172, 353, (1935).

<sup>||</sup> Griffith, McKeown, and Winn, *ibid.*, 28, 107, (1932); *ibid.*, p. 518.

<sup>††</sup> *Trans. Chem. Soc.*, 1693, (1925).

0.08 gram of catalyst per litre of well-stirred solution are given in Table 10, along with those calculated from the equation

$$\ln k' = 20.94 - 16580/RT.$$

*Table 10*

*Decomposition of Hypochlorite Ion at the Surface of Nickel Peroxide*

$t^\circ \text{ C.}$	$k' \times 10^4$ (seconds $^{-1}$ : concentration in gram molecules/litre)	
	Observed	By the Arrhenius equation
25	8.12	7.83
30	12.4	12.4
35	19.4	19.7
40	29.3	30.5
45	45.2	45.1
50	69.2	68.2

*Discussion of the Arrhenius Equation*

We have now examined a variety of chemical changes in the light of the integrated form of the Arrhenius equation

$$k = Ae^{-E_A/RT}, \quad \text{I (4)}$$

and have found quite reasonable agreement for all the reactions considered. This equation is, as already stated, an excellent first approximation to the truth. In point of fact, the first systematic collation of data on the kinetics of reactions in solution showed that not more than one per cent. of the reactions then known exhibited deviations, either genuine or spurious, from the law. This conclusion depended, of course, on an estimate of the likely error in measurement, which is not often easy to assess, and can only be fully appreciated by experimentalists. In any case, so satisfactory has been this very simple formula, that deviations from it have been almost instinctively viewed with distrust. Nevertheless, the general arguments of Trautz (p. 4) and of Berthoud (p. 23) on the very different approaches of thermodynamics and statistics, prove conclusively that the integrated form of the Arrhenius equation can have but a limited applicability, and that it is a special case of a more general relation, a simple example of which is

$$k = BT^{C/R}e^{-E/RT}, \quad \text{I (6)}$$

which again can only cover the facts within relatively narrow regions.

We note that neither  $A$  nor  $E_A$  is a constant, and that both are

functions of the temperature, for, by applying equation I(11) we see that

$$A = B(Te)^{C/R} \quad (19)$$

and that

$$E_A = E + CT. \quad (13)$$

In order to decide whether the value of  $E_A$  determined at one temperature is in fact different from the value of  $E_A$  determined at another temperature, we must, of course, know the accuracy with which the apparent energy of activation can be measured. No general answer can be given. An indication of the order of magnitude of the error in measurement may be gained from an inspection of Table 11, in the second column of which are found the first values calculated for the apparent energies of activation, and in the third column of which are found the values since determined in more recent experiments. Clearly, the error of experiment in these cases does not exceed 100 calories per gram molecule. More precise work can sometimes reduce the error to still lower limits, e.g.  $\pm 45$  calories in the case of the mutarotation of glucose.†

Table 11  
*The Reproducibility of  $E_A$  Values*

Reaction	$E_A$	
	Original value	Repetition
The reaction between ethyl iodide and sodium ethoxide	20,880†	20,980‡
The conversion of ammonium cyanate into urea	23,170§	23,240
The iodination of acetone	20,580††	20,680‡‡

† *The Kinetics of Reaction in Solution*, 1st ed., p. 34, (1933).

‡ Gibson, Fawcett, and Perrin, *Proc. Roy. Soc., A*, **150**, 223, (1935).

§ *Op. cit.*, p. 35.

|| Svirbely and Warner, *J. Amer. Chem. Soc.*, **57**, 1883, (1935).

†† *Op. cit.*, p. 47.

‡‡ G. F. Smith, *Trans. Chem. Soc.*, 1744, (1934), using equation II(1).

Now let us suppose that the apparent energy of activation can be measured to this degree of accuracy at two temperatures differing by  $10^\circ\text{ C}$ . We should still be in doubt as to whether  $E_A$  varies with temperature unless the term,  $dE_A/dT$ , exceeded  $\pm 9$  cals./gm.-mole-degree. Care must therefore be exercised in assessing deviations from the equation of Arrhenius. Particularly dangerous is the temptation to ascribe to the apparent change of activation energy with tempera-

† Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc., A*, **176**, 352, (1940).

ture what is in reality due to the occurrence of concomitant reactions, which, as we have seen, are so seldom absent from reactions in solution. An example may be cited to illustrate the difficulty.

*An Example of an Apparent Deviation from the Equation of Arrhenius*

The bimolecular character of the reaction between hydriodic acid and hydrogen peroxide,



and the accelerating influence of acids have long been established.† Neutral iodides also bring about the decomposition of hydrogen peroxide, by an apparently simple bimolecular process, as Walton's results‡ in Table 12 indicate. With potassium iodide, the constant

Table 12

[NaI] × 10³ (gram mol./litre)	$k_{25^\circ\text{C.}} \times 10^3$ (minutes⁻¹; log.)	$\frac{k_{\text{obs}}}{[\text{NaI}]}$
6.16	8.13	1.32
9.21	11.99	1.30
12.26	16.21	1.32
18.40	24.19	1.31
24.52	31.95	1.30
30.60	39.47	1.29
36.80	48.10	1.31

is 1.33 litres per gram molecule per minute (cf.  $1.31 \pm 0.02$  with NaI). Aqueous solutions of iodides, however, contain the molecular species HOI and OI<sup>-</sup>, both of which attack hydrogen peroxide with different rates, characterized by measurable coefficients.§ When, therefore, it is found that Walton's excellent constants at various temperatures (Table 13) give a falling  $E_A$ ,|| it is natural to suppose that the effects of concurrent reactions have not been completely eliminated. Recent repetitions of this reaction, by Liebhafsky and Mohammad,†† have proved the existence, in acid solution, of a composite rate given by

$$+ \frac{d[\text{I}_3^-]}{dt} = k_0[\text{H}_2\text{O}_2][\text{I}^-] + k_1[\text{H}_2\text{O}_2][\text{I}^-][\text{H}^+].$$

† Harcourt and Esson, *Phil. Trans.*, **157**, 117, (1867).

‡ *Z. physikal. Chem.*, **47**, 185, (1904).

§ Magnanini, *Gazz. chim. ital.*, **21**, 476, (1891); Noyes, *Z. physikal. Chem.*, **19**, 601, (1896); Brode, *ibid.*, **49**, 208, (1904); Abel, *Z. Elektrochem.*, **14**, 598, (1908); *Z. physikal. Chem.*, **96**, pp. 1-180, (1920); *ibid.*, **136**, 161, (1928); Harned, *J. Amer. Chem. Soc.*, **40**, 1461, (1918); Liebhafsky, *ibid.*, **54**, 3499, (1932).

|| *Kinetics*, 1st ed., p. 184.

†† *J. Amer. Chem. Soc.*, **55**, 3977, (1933).

For both velocity coefficients the Arrhenius equation is obeyed to within  $\pm 3$  per cent., the apparent energies of the concomitant reactions being  $13,400 \pm 105$  ( $0\text{--}50^\circ \text{C}$ ) and  $10,450 \pm 120$  ( $0\text{--}40^\circ \text{C}$ ) respectively. Confirmation is afforded by the work of Hender and R. A. Robinson.<sup>†</sup>

Table 13

$t^\circ \text{ C.}$	$k_{\text{obs}} \times 10^3$ (minutes $^{-1}$ g.m./l.)	$E_A$ (calories/gram-mole)
15	6.35	14,240
25	14.12	13,580
35	30.00	12,490
45	62.50	

### *Genuine Deviations from the Integrated Form of the Arrhenius Equation*

Recent work has shown that, even in the absence of complications, the velocity coefficients of certain reactions cannot be reproduced within the experimental accuracy by the equation

$$k = Ae^{-E/RT}. \quad \text{I (4)}$$

How general this conclusion may be cannot yet be decided: we shall have to wait until many more chemical reactions have been studied with greater thoroughness. Nor can we say what is the exact expression for the dependence of  $k$  on  $T$ . Both thermodynamic and statistic considerations point in the direction of an equation of the form

$$k = BT^{C/R}e^{-E/RT}, \quad \text{I (6)}$$

and it is in the light of this admittedly inadequate relationship that we shall now examine some recent results. It will be found capable, with one exception, of accommodating the facts.

The first proven instance of the failure of equation I (4) is provided, somewhat ironically, by the hydrolysis of sucrose.<sup>‡</sup> Semerano<sup>§</sup> had, however, emphasized its inapplicability to the kinetics of the saponification of amides, but as this reaction is not free from complications, his conclusion, though possibly correct, is not free from objections. His results, which refer to aqueous alcoholic solutions of sodium carbonate at temperatures about  $100^\circ \text{C.}$ , certainly do not conform to equation I (4), but a detailed examination shows that  $dE_A/dT$  is

<sup>†</sup> *Trans. Faraday Soc.*, **29**, 1300, (1933).

<sup>‡</sup> Moelwyn-Hughes, *Z. physikal. Chem.*, **B**, **26**, 281, (1934).

<sup>§</sup> *Gazz. chim. ital.*, **61**, 921, (1931).

as often positive as it is negative, so that the deviations are erratic, and, to some extent, attributable to experimental errors.

### *The Inversion of Cane Sugar*

It is apparent from a perusal of the complete works of Arrhenius† that he had no direct acquaintance with experiments on the inversion of cane sugar. In his fundamental paper‡ he relied on the results of Urech§ and of Spohr|| and ascribed to the hydrolysis of sucrose, catalysed by strong acids, an energy of activation of 25,400 calories, which has since been faithfully reproduced by scores of investigators. Arrhenius concluded that 'the excellent agreement of the constant ( $E_A$ ) for the two (sets of data) shows that the equation I (4) holds over the whole range of temperature from 1 to 55° C.' A close inspection of the data, which are, by later standards, of only moderate accuracy, nevertheless reveals a definite trend of  $E_A$  with respect to temperature. Urech's data, for example, yield the following values:

Temperature range (°C.)	$E_A$ (calories/gram-mole)
1–10	27,200
10–20	26,000
20–30	23,200
30–40	20,500

Many subsequent workers have arrived at a value of  $25,400 \pm 200$  calories, and this is doubtless correct at 25° C., to which much of the work refers. Only in one case has it been emphatically claimed that a constant value of the apparent energy of activation covers a wide temperature range. R. F. Jackson and C. L. Gibbs†† find  $E_A/R$  to be 12925·2 using  $N/100$  hydrochloric acid and 12940·05 using  $N/10$  acid, for the temperature range 30–90·3° C. Their claim, however, cannot be substantiated.‡‡

The very marked change of the apparent energy of activation with respect to temperature is too serious a matter to go unverified. This familiar reaction was therefore reinvestigated, using the polarimetric

† Riesenfeld, *A Biography of Svante Arrhenius*, Leipzig, (1932).

‡ *Z. physikal. Chem.*, **4**, 226, (1889).

§ *Berichte*, **16**, 762, (1883).

|| *Z. physikal. Chem.*, **2**, 195, (1888).

†† *Bureau of Standards*, **31A**, 375, (1920).

‡‡ I am indebted to Dr. Martin Kilpatrick, of the University of Pennsylvania, for his attempt to procure a copy of this regrettably unavailable publication from the Superintendent of Documents, U.S. Government Printing Office.

method, which is the most accurate one available in the present case. The effect, which has escaped attention for so long, has been amply confirmed† in a series of experiments (Table 14) carried out with solutions of 5 per cent. sucrose, by weight, in approximately *N*/5 hydrochloric acid. The velocity data have been arbitrarily divided into three temperature regions, for each of which reasonably constant values of  $E_A$  were found. As a first approximation these results are summarized by the equation

$$E_A = 52400 - 46RT.$$

Table 14

*Unimolecular Velocity Coefficients for the Hydrolysis of Sucrose by Hydrochloric Acid*

$t^\circ C.$	$k \times 10^6$ (sec. <sup>-1</sup> )	$[HCl] \times 10$ (g.-mole/litre)	$\frac{k}{[HCl]} \times 10^6$ observed	$\frac{k}{[HCl]} \times 10^6$ calculated	The Arrhenius equations
15.45	6.82	1.907	3.58	3.58	
19.40	12.5	1.905	6.51	6.66	$\ln k/[HCl]$
23.09	22.0	1.904	11.5	11.3	$= 34.19 - 25430/RT.$
27.26	39.0	1.902	20.5	20.6	
31.08	65.2	1.901	34.3	34.1	$\ln k/[HCl]$
35.98	123	1.897	64.8	65.0	$= 32.55 - 24470/RT.$
41.00	235	1.893	124	124	
46.10	411	1.889	218	225	$\ln k/[HCl]$
51.15	738	1.886	391	391	$= 30.12 - 22950/RT.$
57.10	1,410	1.880	750	745	

The gradient  $dE_A/dT$ , however, is not constant, which means that equation I(6), though more satisfactory than equation I(4), is still inadequate to cope with the facts.

The reaction has since been further studied by many investigators,‡ and particularly by Leininger and Kilpatrick,§ whose results, except in points of detail, confirm those already discussed. Leininger and Kilpatrick have combined with a study of the temperature effect a simultaneous study of the concentration effects of sucrose and catalyst. The decrease in  $E_A$  with rise in temperature is well shown in their graph, which is reproduced here (Fig. 6). Their conclusions

† Moelwyn-Hughes, *Z. physikal. Chem.*, **B**, *26*, 281, (1934).

‡ e.g. Hitchcock and Dougan, *J. Phys. Chem.*, **39**, 1177, (1935); Sturtevant, *J. Amer. Chem. Soc.*, **59**, 1528, (1937); Pearce and Thomas, *J. Phys. Chem.*, **42**, 455, (1938); Heidt and Purves, *J. Amer. Chem. Soc.*, **60**, 1206, (1938); Duboux, *Helv. Chim. Acta*, **21**, 236, (1938).

§ *J. Amer. Chem. Soc.*, **60**, 2891, (1938).

differ from ours chiefly in the sign of  $d^2E_A/dT^2$ , about which there still remains some obscurity. Individual estimates of  $dE_A/dT$  are as follows:

$t^\circ \text{ C.}$	$dE_A/dT$ (cal./gm. mole degree)
12.51	-58
27.75	-79
41.59	-90

The first value is obtained from the data of Leininger and Kilpatrick (*loc. cit.*), who also find a value of about -70 at  $10^\circ \text{ C.}$ , and smaller values at higher temperatures. There no longer remains any doubt

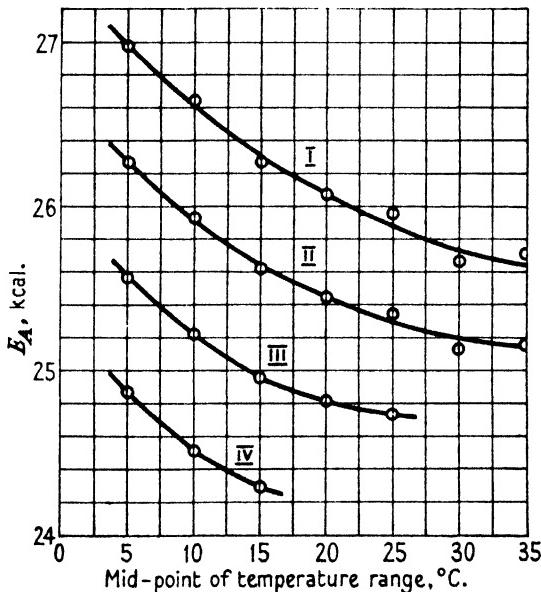


FIG. 6. Effect of temperature on energy of activation:  
I, 0 molar HCl; II, 1 molar HCl; III, 2 molar HCl; IV, 3 molar HCl.

that the Arrhenius energy of activation for the inversion of cane sugar shows a decrease as the temperature is raised, and there is general agreement concerning its order of magnitude. It is not without interest that the reaction first used to measure the dependence of chemical change on time should have proved to provide also the first demonstration of the dependence of critical energy on temperature.

*More Exact Representations of the Dependence of Reaction Velocity upon Temperature*

The glycosides—particularly sucrose—are complicated structures, which, moreover, hydrolyse only in the presence of catalysts; and the questions arise as to how far high values of  $-dE_A/dT$  are specific to changes suffered by large molecules, or to catalysis. The experimental investigation of the uncatalysed hydrolysis of a suitable and simple molecule should allow of a decision. Ethyl iodide appeared to be a favourable case,



but its study is complicated† by a side reaction,  $\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$ , which incidentally leads to occasional explosions; and the work was consequently abandoned.

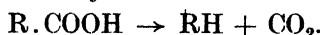
The uncatalysed hydrolysis of three methyl halides has been found to be free from complications, and to proceed unimolecularly to completion at all accessible concentrations and temperatures.‡ The results in condensed form are shown in Table 15, with energies in calories per gram molecule, and velocity constants in reciprocal seconds. These figures show beyond doubt that high values of  $-dE_A/dT$  are not specific to the catalysed hydrolysis of glycosides, but hold also for the uncatalysed hydrolysis of methyl halides.

Table 15

	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{Br}$	$\text{CH}_3\text{I}$
$k_{298.1}$	$1.99 \times 10^{-6}$	$3.57 \times 10^{-7}$	$6.87 \times 10^{-8}$
$k_{273.1}$	$1.08 \times 10^{-4}$	$1.31 \times 10^{-3}$	$4.47 \times 10^{-4}$
$E_{298.1}$	27,703	26,525	28,147
$E_{273.1}$	22,706	21,424	23,111
$dE_A/dT$	-66.62	-68.01	-67.14

Though it is too early yet to generalize, we may now say that a marked fall in the apparent energy of activation with rise in temperature characterizes both simple and complicated hydrolyses in solution.

Entirely analogous results have been found§ for the elimination of carbon dioxide from carboxylic acids in water:



† Moelwyn-Hughes, *Trans. Chem. Soc.*, 1576, (1933). A further discrepancy, thought at the time to be due to the formation of a stable iodo-ether, has since been shown to be due to a fault in my technique. See Greenspan, Liotta, and La Mer, *Trans. Faraday Soc.*, 31, 824, (1935), and Eagle and Warner, *J. Amer. Chem. Soc.*, 61, 488, (1939).

‡ *Idem, Proc. Roy. Soc., A*, 164, 295, (1938).

§ Dinglinger and Schröer, *Z. physikal. Chem.*, A, 179, 401, (1937); P. Johnson and Moelwyn-Hughes, *Proc. Roy. Soc., A*, 175, 118, (1940).

Attempts to study these reactions in other solvents have, unfortunately, not proved successful. Tribromacetic acid in toluene, for example, attacks the solvent, forming benzyl bromide and at least one of the bromotoluenes. Dinglinger and Schröer's data on the decomposition of oxalic acid in dioxan solution yield the approximate equation

$$E_A = 52850 - 57T,$$

and early work† on the decomposition of malonic acid in water leads to the rough relation

$$E_A = 58750 - 76.5T$$

within the temperature region 350–415°K. True energies of activation in solution thus lie fairly close to those found for comparable gas reactions.

Even the mutarotation of glucose, long regarded as an example of a constancy in  $E_A$  (see p. 40) follows the same trend. G. F. Smith and M. C. Smith‡ pointed out that the apparent energies of activation calculated from the classical experiments of Hudson and Dale§ show, with one exception, a steady fall as the temperature is raised. From their own experiments, they deduce a value of –29 calories/gram-mole-degree for the constant  $C$ . Kendrew and Moelwyn-Hughes|| obtained somewhat lower values for glucose, and certain other hexoses and pentoses (Table 16). Because of the slight differences

Table 16

*Kinetic Data for the Mutarotation of α-Sugars in Water at 298.1° K.*

Sugar	$k \times 10^{-4}$ sec. <sup>-1</sup>	$E_A$ cal./g.mol.	$\frac{dE_A}{dT}$
Xylose	8.578	16,245	$-20.4 \pm 8.4$
Mannose	4.572	16,375	$-20.5 \pm 2.8$
Glucose	1.463	16,945	$-19.6 \pm 5.9$
Lactose	1.869	17,225	$-21.9 \pm 5.6$

in the values of  $dE_A/dT$  a mean value of –20.5 was adopted in formulating the kinetic results. These experiments supplement and extend, but do not contradict, the earlier work (Table 17).

† e.g. by Bernoulli and Jakubowicz, *Helv. Chim. Acta*, **4**, 1018, (1921).

‡ *Trans. Chem. Soc.*, 1413, (1937).

§ *J. Amer. Chem. Soc.*, **39**, 320, (1917).

|| *Proc. Roy. Soc., A*, **176**, 352, (1940).

Table 17

*A Comparison of Certain Apparent Energies of Activation obtained from Early and More Recent Work*

Reaction (in water)	T° K.	E <sub>A</sub> (cal./gm.-mole)	Observers
The mutarotation of α-mannose	293.35	16,460 ± 320	Hudson and Sawyer, <i>J. Amer. Chem. Soc.</i> , <b>39</b> , 470, (1917).
	293.35	16,525 ± 45	Kendrew and Moelwyn-Hughes, <i>loc. cit.</i> , (1940).
The mutarotation of α-lactose	294.17	16,880 ± 670	Hudson, <i>Z. physikal. Chem.</i> <b>44</b> , 487, (1903).
	294.17	17,033 ± 110	Kendrew and Moelwyn-Hughes, <i>loc. cit.</i> , (1940).

The kinetics of the decomposition of diazonium salts† are not quite so simple to interpret, chiefly because we can never be sure of the part played by free radicals.‡ In water, however, as distinct from non-aqueous solvents, there is no definite evidence in favour of decomposition by a free radical mechanism, nor against the assumption that the rate is determined primarily by the interaction of the cation with water:



Recent kinetic data, a specimen of which is shown in Table 18,§ have accordingly to be interpreted on this supposition.

When the apparent energy of activation changes only slightly with respect to temperature, it is not easy to determine the value of the constant *C*. Three methods are available and have been described in detail in the papers referred to above. When applied to the rate of evolution of nitrogen from diazoacetic ester in aqueous acidic solution,||



they yield an average value of  $-4.615$  for *C/R*. A disinterested analysis of the data, however, shows that in this case the simple

† Cain and Nicoll, *Trans. Chem. Soc.*, **81**, 1412, (1902); Saunders, *The Diazo-Compounds and their Technical Applications*, Arnold, (1936).

‡ Waters, *Trans. Chem. Soc.*, **2007**, (1937); Hey and Waters, *Chem. Rev.*, **21**, 169, (1937).

§ Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948, (1940).

|| *Idem, ibid.*, **37**, 283, (1941).

formula of Arrhenius is actually slightly more competent to reproduce the facts.

A summary of some of these results, giving the constants of equation I (6), is found in Tables 19 and 20. Future work, it is to be hoped, will be characterized by still more accurate data and more comprehensive formulae. In the meantime they serve to move the subject from the artificial simplicity in which it had its origin.

Table 18

*The Unimolecular Decomposition of Benzene Diazonium Chloride  
in Water*

$$T = 313.14 \pm 0.03^\circ \text{ K.} \quad k = 4.240 \times 10^{-4} \text{ sec.}^{-1}$$

<i>t</i> (secs.)	$(p_\infty - p_t)_{\text{obs}}$	$(p_\infty - p_t)_{\text{cal}}$	<i>t</i> (secs.)	$(p_\infty - p_t)_{\text{obs}}$	$(p_\infty - p_t)_{\text{cal}}$
0	22.62	22.68	1140	13.98	13.98
30	22.33	22.39	1200	13.62	13.63
60	22.08	22.10	1260	13.28	13.28
90	21.80	21.82	1320	12.96	12.95
120	21.55	21.55	1380	12.62	12.63
150	21.24	21.27	1440	12.30	12.31
180	20.97	21.00	1500	12.00	12.00
210	20.72	20.74	1560	11.74	11.70
240	20.47	20.47	1620	11.41	11.40
270	20.23	20.22	1680	11.10	11.12
300	19.97	19.96	1740	10.83	10.83
330	19.72	19.71	1800	10.54	10.57
360	19.45	19.46	1920	10.03	10.04
390	19.18	19.22	2040	9.53	9.54
420	18.97	18.97	2160	9.05	9.07
450	18.64	18.74	2280	8.61	8.62
480	18.48	18.49	2400	8.15	8.19
510	18.25	18.27	2520	7.76	7.79
540	18.05	18.03	2640	7.40	7.40
570	17.82	17.80	2760	7.00	7.03
600	17.60	17.58	2880	6.67	6.69
630	17.35	17.36	3000	6.34	6.35
660	17.12	17.14	3120	6.04	6.04
690	16.92	16.92	3240	5.77	5.74
720	16.73	16.70	3420	5.33	5.32
750	16.53	16.50	3600	4.88	4.88
780	16.32	16.29	3840	4.43	4.45
810	15.99	16.08	4080	4.02	4.02
840	15.90	15.88	4320	3.64	3.63
870	15.65	15.68	4560	3.32	3.28
900	15.49	15.47	4800	2.98	2.86
960	15.10	15.09	5100	2.62	2.61
1020	14.77	14.71	5400	2.32	2.30
1080	14.36	14.34			

Table 19

*Experimental Velocity Coefficients for Certain Reactions in Water, compared with those reproduced by Equation I (6). See Table 20*

*The Hydrolysis of Methyl Chloride*

T° K.	$k_{\text{observed}}$	$k_{\text{formula}}$
314.78	$2.30 \times 10^{-7}$	$2.21 \times 10^{-7}$
326.24	$9.58 \times 10^{-7}$	$9.60 \times 10^{-7}$
333.11	$2.16 \times 10^{-6}$	$2.18 \times 10^{-6}$
341.28	$5.43 \times 10^{-6}$	$5.40 \times 10^{-6}$
348.99	$1.22 \times 10^{-5}$	$1.20 \times 10^{-5}$
357.30	$2.69 \times 10^{-5}$	$2.70 \times 10^{-5}$
373.37	$1.08 \times 10^{-4}$	$1.10 \times 10^{-4}$
383.98	$2.48 \times 10^{-4}$	$2.54 \times 10^{-4}$

*The Hydrolysis of Methyl Bromide*

290.13	$1.07 \times 10^{-7}$	$1.04 \times 10^{-7}$
308.83	$1.65 \times 10^{-6}$	$1.65 \times 10^{-6}$
319.50	$6.71 \times 10^{-6}$	$6.57 \times 10^{-6}$
330.70	$2.47 \times 10^{-5}$	$2.46 \times 10^{-5}$
335.02	$3.91 \times 10^{-5}$	$3.94 \times 10^{-5}$
350.27	$1.84 \times 10^{-4}$	$1.84 \times 10^{-4}$
363.38	$6.06 \times 10^{-4}$	$6.12 \times 10^{-4}$
373.18	$1.28 \times 10^{-3}$	$1.31 \times 10^{-3}$

*The Hydrolysis of Methyl Iodide*

308.87	$3.43 \times 10^{-7}$	$3.53 \times 10^{-7}$
321.23	$1.93 \times 10^{-6}$	$1.92 \times 10^{-6}$
323.69	$2.70 \times 10^{-6}$	$2.64 \times 10^{-6}$
328.72	$4.81 \times 10^{-6}$	$4.925 \times 10^{-6}$
333.88	$8.72 \times 10^{-6}$	$9.08 \times 10^{-6}$
342.92	$2.49 \times 10^{-5}$	$2.50 \times 10^{-5}$
363.06	$1.80 \times 10^{-4}$	$1.84 \times 10^{-4}$
372.92	$4.31 \times 10^{-4}$	$4.34 \times 10^{-4}$

*The Decomposition of Trichloracetic Acid*

323.15	$6.03 \times 10^{-7}$	$6.13 \times 10^{-7}$
328.11	$1.42 \times 10^{-6}$	$1.44 \times 10^{-6}$
332.78	$3.23 \times 10^{-6}$	$3.18 \times 10^{-6}$
338.25	$7.75 \times 10^{-6}$	$7.67 \times 10^{-6}$
343.11	$1.63 \times 10^{-5}$	$1.63 \times 10^{-5}$
348.30	$3.56 \times 10^{-5}$	$3.61 \times 10^{-5}$
353.07	$7.19 \times 10^{-5}$	$7.29 \times 10^{-5}$
358.03	$1.47 \times 10^{-4}$	$1.48 \times 10^{-4}$
363.14	$2.96 \times 10^{-4}$	$2.97 \times 10^{-4}$
368.02	$5.96 \times 10^{-4}$	$5.76 \times 10^{-4}$
373.13	$1.10 \times 10^{-3}$	$1.12 \times 10^{-3}$

Table 19 (*continued*)*The Decomposition of Tribromacetic Acid*

T° K.	$k_{\text{observed}}$	$k_{\text{formula}}$
297.91	$4.89 \times 10^{-7}$	$4.97 \times 10^{-7}$
302.98	$1.28 \times 10^{-6}$	$1.29 \times 10^{-6}$
308.10	$3.25 \times 10^{-6}$	$3.25 \times 10^{-6}$
313.10	$7.65 \times 10^{-6}$	$7.77 \times 10^{-6}$
317.87	$1.77 \times 10^{-5}$	$1.74 \times 10^{-5}$
322.82	$4.06 \times 10^{-5}$	$3.89 \times 10^{-5}$
327.97	$8.44 \times 10^{-5}$	$8.75 \times 10^{-5}$
333.03	$1.86 \times 10^{-4}$	$1.89 \times 10^{-4}$
338.12	$4.12 \times 10^{-4}$	$4.00 \times 10^{-4}$
343.12	$8.17 \times 10^{-4}$	$8.15 \times 10^{-4}$

*The Decomposition of Trinitrobenzoic Acid*

328.05	$8.95 \times 10^{-7}$	$8.75 \times 10^{-7}$
333.13	$2.09 \times 10^{-6}$	$2.12 \times 10^{-6}$
338.10	$4.94 \times 10^{-6}$	$4.81 \times 10^{-6}$
343.10	$1.01 \times 10^{-5}$	$1.07 \times 10^{-5}$
346.12	$1.73 \times 10^{-5}$	$1.73 \times 10^{-5}$
349.91	$3.03 \times 10^{-5}$	$3.10 \times 10^{-5}$
357.98	$1.03 \times 10^{-4}$	$9.68 \times 10^{-6}$
363.10	$2.12 \times 10^{-4}$	$2.05 \times 10^{-4}$
368.29	$4.05 \times 10^{-4}$	$4.11 \times 10^{-4}$
373.27	$7.44 \times 10^{-4}$	$7.91 \times 10^{-4}$

*The Mutarotation of  $\alpha$ -Xylose*

273.45	$6.94 \times 10^{-5}$	$6.94 \times 10^{-5}$
278.03	$1.16 \times 10^{-4}$	$1.15 \times 10^{-4}$
283.03	$1.97 \times 10^{-4}$	$1.96 \times 10^{-4}$
287.96	$3.29 \times 10^{-4}$	$3.23 \times 10^{-4}$
293.06	$5.24 \times 10^{-4}$	$5.23 \times 10^{-4}$
298.09	$8.43 \times 10^{-4}$	$8.55 \times 10^{-4}$
303.17	$1.349 \times 10^{-3}$	$1.352 \times 10^{-3}$
308.17	$2.077 \times 10^{-3}$	$2.084 \times 10^{-3}$

*The Mutarotation of  $\alpha$ -Mannose*

273.41	$3.610 \times 10^{-5}$	$3.620 \times 10^{-5}$
278.05	$6.115 \times 10^{-5}$	$6.054 \times 10^{-5}$
283.09	$1.068 \times 10^{-4}$	$1.043 \times 10^{-4}$
288.09	$1.753 \times 10^{-4}$	$1.738 \times 10^{-4}$
293.13	$2.849 \times 10^{-4}$	$2.857 \times 10^{-4}$
298.12	$4.552 \times 10^{-4}$	$4.581 \times 10^{-4}$
303.06	$7.176 \times 10^{-4}$	$7.176 \times 10^{-4}$
308.12	$1.115 \times 10^{-3}$	$1.117 \times 10^{-3}$

Table 19 (continued)

*The Mutarotation of  $\alpha$ -Glucose*

T° K.	$k_{\text{observed}}$	$k_{\text{formula}}$
273.32	$1.052 \times 10^{-5}$	$1.051 \times 10^{-5}$
278.26	$1.864 \times 10^{-5}$	$1.857 \times 10^{-5}$
283.12	$3.195 \times 10^{-5}$	$3.177 \times 10^{-5}$
288.15	$5.451 \times 10^{-5}$	$5.417 \times 10^{-5}$
293.13	$9.028 \times 10^{-5}$	$8.995 \times 10^{-5}$
298.06	$1.436 \times 10^{-4}$	$1.457 \times 10^{-4}$
303.07	$2.335 \times 10^{-4}$	$2.336 \times 10^{-4}$
308.16	$3.681 \times 10^{-4}$	$3.702 \times 10^{-4}$
313.14	$5.682 \times 10^{-4}$	$5.711 \times 10^{-4}$
318.19	$8.738 \times 10^{-4}$	$8.720 \times 10^{-4}$
323.13	$1.296 \times 10^{-3}$	$1.299 \times 10^{-3}$

*The Mutarotation of  $\alpha$ -Lactose*

288.04	$6.77 \times 10^{-5}$	$6.73 \times 10^{-5}$
293.19	$1.148 \times 10^{-4}$	$1.148 \times 10^{-4}$
298.11	$1.879 \times 10^{-4}$	$1.872 \times 10^{-4}$
303.28	$3.065 \times 10^{-4}$	$3.068 \times 10^{-4}$
308.18	$4.819 \times 10^{-4}$	$4.814 \times 10^{-4}$
313.21	$7.496 \times 10^{-4}$	$7.511 \times 10^{-4}$
318.12	$1.138 \times 10^{-3}$	$1.144 \times 10^{-3}$
322.23	$1.603 \times 10^{-3}$	$1.601 \times 10^{-3}$

*The Decomposition of the Benzene Diazonium Ion*

288.16	$9.30 \times 10^{-6}$	$9.20 \times 10^{-6}$
292.99	$2.01 \times 10^{-5}$	$2.05 \times 10^{-5}$
297.80	$4.35 \times 10^{-5}$	$4.41 \times 10^{-5}$
303.07	$9.92 \times 10^{-5}$	$9.88 \times 10^{-5}$
308.13	$2.07 \times 10^{-4}$	$2.08 \times 10^{-4}$
313.20	$4.28 \times 10^{-4}$	$4.26 \times 10^{-4}$
317.99	$8.18 \times 10^{-4}$	$8.16 \times 10^{-4}$
322.98	$1.58 \times 10^{-3}$	$1.57 \times 10^{-3}$
328.20	$3.01 \times 10^{-3}$	$3.03 \times 10^{-3}$
333.17	$5.64 \times 10^{-3}$	$5.54 \times 10^{-3}$

*Units*

The choice of the most appropriate units in which to express the quantities with which we have to deal in chemical kinetics is arbitrary, and determined by convenience. For theoretical purposes, a time unit of one second, and a concentration unit of one molecule per c.c., with  $\ln_e$ , are most appropriate. Experimentally, one gram molecule per litre is a more suitable concentration unit. The conversion factor from the former to the latter is simply  $(N_0/1000)^{n-1}$ , where  $N_0$  is the Avogadro number, and  $n$  the order of reaction. In the present work, all velocity constants, unless otherwise stated, are expressed in these experimental units. Occasionally, velocity coeffi-

cients are expressed in terms of molar fractions,  $N$ , of the reactants in solution,

$$k_N = -\frac{1}{N^n} \frac{dN}{dt}, \quad (20)$$

rather than in terms of concentrations,  $c$ , with the usual unit of one gram molecule per litre,

$$k_c = -\frac{1}{c^n} \frac{dc}{dt}. \quad (21)$$

In dilute solution, we may use the approximate equation

$$c = \left( \frac{1000}{V_s} \right) N \quad (22)$$

to find the relation between the constants, which is seen to be

$$k_c = \left( \frac{V_s}{1000} \right)^{n-1} k_N, \quad (23)$$

where  $V_s$  is the molar volume of the solvent.

*Table 20*

*The Influence of Temperature on the Velocity Coefficients of Certain Reactions in Water*

$k$  is given in seconds<sup>-1</sup>, except in the case of the catalytic reaction, for which  $k$  is in the units of seconds<sup>-1</sup> × litres/gram mole.  $E$  is in calories per gram mole.

$$\ln_e k = \ln_e B + (C/R) \ln_e T - E/RT$$

Reaction	Reference	$\ln_e B$	$-(C/R)$	$E$
$\text{CH}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}^+ + \text{Cl}^-$	1	253.798	33.559	47,595
$\text{CH}_3\text{Br} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}^+ + \text{Br}^-$	1	259.399	34.259	46,720
$\text{CH}_3\text{I} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}^+ + \text{I}^-$	1	257.565	33.821	48,195
$\text{CCl}_3\text{COOH} \rightarrow \text{CCl}_3\text{H} + \text{CO}_2$	2	110.824	10.066	42,910
$\text{CBr}_3\text{COOH} \rightarrow \text{CBr}_3\text{H} + \text{CO}_2$	2	109.862	10.066	39,610
$1:3:5-\text{C}_6\text{H}_3(\text{NO}_2)_3\text{COOH}$ → $1:3:5-\text{C}_6\text{H}_3(\text{NO}_2)_3 + \text{CO}_2$	2	197.728	22.648	52,300
$\alpha$ -Xylose → $\beta$ -Xylose	3	89.537	10.318	22,355
$\alpha$ -Mannose → $\beta$ -Mannose	3	89.055	10.318	22,485
$\alpha$ -Glucose → $\beta$ -Glucose	3	88.879	10.318	23,055
$\alpha$ -Lactose → $\beta$ -Lactose	3	89.594	10.318	23,335
$\text{C}_6\text{H}_5\text{N}_3^+ + \text{H}_2\text{O} \rightarrow \text{N}_3^- + \text{C}_6\text{H}_5\text{OH} + \text{H}^+$	4	157.067	18.000	38,200
$\text{N}_3^-\text{CHCOOC}_6\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{N}_3^- + \text{HOCH}_2\text{COOC}_6\text{H}_5$	5	44.680	4.615	18,890

1. Moelwyn-Hughes, *Proc. Roy. Soc., A*, **164**, 295, (1938).
2. P. Johnson and Moelwyn-Hughes, *ibid.*, **175**, 118, (1940).
3. Kendrew and Moelwyn-Hughes, *ibid.*, **176**, 352, (1940).
4. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948, (1940).
5. *Idem*, *ibid.*, **37**, 283, (1941).

### III

#### A SURVEY OF BIMOLECULAR REACTIONS

THE vast majority of chemical reactions occur in liquid systems. Most of these are bimolecular.

According to the collision theory in its simplest form, the number of molecules decomposing in a bimolecular reaction is equal to the number of activating collisions. The expression given by the kinetic theory of gases for the total number of collisions occurring per c.c. per second between molecules of types *A* and *B* is

$$_A Z_B = n_A n_B (r_A + r_B)^2 \left\{ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{\frac{1}{2}}. \quad (21)$$

The Boltzmann term  $e^{-E/RT}$  gives the fraction of this number which has energies of *E* or more, distributed in two quadratic terms; hence the anticipated rate of chemical change becomes

$$\frac{dn}{dt} = n_A n_B (r_A + r_B)^2 \left\{ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{\frac{1}{2}} e^{-E/RT}.$$

The bimolecular velocity constant, expressed in litres per gram molecule per second, is defined as

$$k = \frac{dn}{dt} \frac{1}{n_A n_B} \frac{N_0}{1000},$$

$N_0$  being the Avogadro constant. Combining, we have

$$k = \frac{N_0}{1000} (r_A + r_B)^2 \left\{ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{\frac{1}{2}} e^{-E/RT} \quad (1)$$

This expression gives the theoretical value of the velocity coefficient of an uncomplicated bimolecular reaction.

On applying the Arrhenius equation (I(11)), it is seen that the true critical increment is related as follows to the apparent value,  $E_A$ :

$$E = E_A - \frac{1}{2} RT. \quad (2)$$

The difference is not important enough to matter except when the temperature of investigation is high or the energy of activation is low.

The first and second attempts to apply equation (1) to reactions in solution† were not very encouraging, for theory exceeded experi-

† Christiansen, *Z. physikal. Chem.*, **113**, 35, (1924); Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 81, (1929).

mental requirements in the first set of changes examined, and fell short of them in the second. The third attempt, however, proved more fruitful.<sup>†</sup> Viewed in retrospect, perhaps the lessons to be learnt from the course in which the subject has developed are, first, the danger of generalizing from scanty information, and, second, the folly of entering any physicochemical field without having read the first few volumes of the *Zeitschrift für physikalische Chemie*.

The comparison between experimental and theoretical rates may be made in various ways.

(1) Using the Arrhenius value of  $E$ , we may substitute directly into equation (1), and calculate the value of  $k$  at any temperature.

The critical increment for the reaction between methyl iodide and sodium ethylate in ethylalcoholic solution is found to be 19,500 calories (Table II 2):



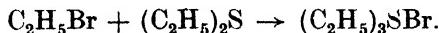
Taking the molecular radii as  $2.64 \times 10^{-8}$  and  $2.74 \times 10^{-8}$  cm. respectively (equation I (17)), the calculated value of  $k$  at 18° C. becomes  $4.12 \times 10^{-4}$  litres/gram molecule-second. The value observed by Hecht and Conrad<sup>‡</sup> is  $4.96 \times 10^{-4}$ , and is subject to a correction due to a dilution effect.

(2) The observed energy of activation may be compared with that given by the relation

$$\frac{\text{number of molecules reacting}}{\text{total number of collisions}} = e^{-E/RT}. \quad \text{I (35)}$$

To evaluate separately the two quantities on the left-hand side of the equation we must choose an arbitrary concentration. One gram molecule per litre is as convenient a unit as any.<sup>§</sup>

The velocity constant for the combination of ethyl bromide and diethyl sulphide in benzylalcoholic solution at 80° C. is  $2.44 \times 10^{-5}$  litres/gram molecule-second (p. 164):



The number of molecules combining per c.c. per second is therefore  $2.44 \times 10^{-5} \times 6.06 \times 10^{20} = 1.48 \times 10^{16}$ . Equation I(21) gives the

<sup>†</sup> *Chem. Rev.*, **10**, 241, (1932).

<sup>‡</sup> *Z. physikal. Chem.*, **3**, 450, (1889).

<sup>§</sup> The consistent use of the molar unit avoids the confusion which may arise from the adoption of the terms 'normal' or 'equivalent'.

total number of collisions as  $1.59 \times 10^{32}$ , hence  $E = 25,800$  calories. The experimental value is 25,470 calories

(3) The constant  $A$  of the Arrhenius equation may be compared with the theoretical value, which is nearly

$$Z = \frac{N_0}{1000} (r_A + r_B)^2 \left\{ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{\frac{1}{2}}. \quad (3)$$

The velocity of the following reaction has been measured very carefully at intervals of  $10^\circ$  between  $70^\circ$  and  $130^\circ$  C.:†



By plotting  $\ln k$  against  $1/T$  in the usual way, it is found that  $A$  is  $4.55 \times 10^{11}$ . The theoretical value of  $Z$  is  $2.86 \times 10^{11}$ . The justification of including ionic reactions among those which can be analysed in this way must be postponed until Chapter IV.

This is the method of comparison most commonly used in the present book.

Some examples are given in Table 1. In many of these, theory and observation are in excellent harmony, and in all of them the difference is no greater than can be allowed for by error in calculation or experiment. The absolute velocities, compared at a temperature of  $25^\circ$  C., differ by a factor of  $10^{11}$ .

It is evident that the theoretical collision frequency varies but slightly from reaction to reaction, the average value being about  $2.77 \times 10^{11}$ . A figure not very different from this is found for all systems of molecules over a very wide range of temperature. For rough calculations, therefore, this is a useful quantity to remember. Its approximate constancy is due to the compensating influence of two rival factors. The effect on the collision frequency caused by the rapidity of light molecules is cancelled by their small cross-sectional area; on the other hand, the effect due to the slower velocity of heavy molecules is almost exactly balanced by their greater collisional diameter. In a pair of ideal bimolecular reactions, therefore, the difference in velocity is given by the term  $e^{(E_1 - E_2)/RT}$  or  $e^{\Delta E/RT}$ .

Two slight corrections have been made in the entries of Table 1 given in the first edition of this work. The first refers to the value of  $E$  for the formation of triethylsulphonium bromide, which was formerly given as 24,470 calories. The second is the omission of the data for the saponification of phthalide: it is clear from the original

† Schwab, quoted by van 't Hoff, *Studies in Chemical Dynamics*, pp. 15, 129, (1896).

Table 1

*Reactions with Velocities agreeing with the Predictions of the Simple Collision Theory*

Reference	Reaction	Solvent	$E_A$ (calories)	$A \times 10^{-11}$	$Z \times 10^{-11}$	$\frac{k_{\text{calc}}}{k_{\text{obs}}}$
				Observed	Calculated	
(1)	$\text{CH}_3\text{ONa} + 1:2:4\text{-ClC}_2\text{H}_4(\text{NO}_2)_2$	$\text{CH}_3\text{OH}$	17,450	1.91	2.42	1.3
(1)	$\text{C}_2\text{H}_5\text{ONa} + 1:2:4\text{-ClC}_2\text{H}_4(\text{NO}_2)_2$	$\text{C}_2\text{H}_5\text{OH}$	16,780	1.80	2.39	1.3
(2)	$\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	19,490	2.42	1.93	0.8
(3)	$\text{C}_2\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	20,650	1.49	2.23	1.5
(3)	$\text{C}_2\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{CH}_3\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	19,900	0.15	2.17	14.5
(4)	$\text{C}_2\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	22,450	3.58	2.31	0.7
(4)	$\text{C}_2\text{H}_5\text{ONa} + \text{iso-C}_3\text{H}_8\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	22,100	1.74	2.31	1.3
(4)	$\text{C}_2\text{H}_5\text{ONa} + \text{C}_4\text{H}_8$	$\text{C}_2\text{H}_5\text{OH}$	22,430	2.78	2.92	1.0
(5)	$\text{C}_2\text{H}_5\text{CH}_3\text{ONa} + \text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	21,560	2.92	2.43	0.8
(5)	$\text{C}_2\text{H}_5\text{CH}_3\text{ONa} + \text{iso-C}_3\text{H}_8\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	21,350	2.45	2.43	1.0
(5)	$\text{C}_2\text{H}_5\text{CH}_3\text{ONa} + \text{C}_4\text{H}_8\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	21,090	1.26	3.12	2.5
(6)	$\alpha\text{-CH}_2\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	20,240	1.30	1.99	1.5
(6)	$m\text{-CH}_2\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	20,510	2.27	1.99	0.9
(6)	$p\text{-CH}_2\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	21,220	8.49	1.99	0.2
(7)	$\beta\text{-C}_1\text{H}_2\text{ONa} + \text{C}_2\text{H}_5\text{I}$	$\text{CH}_3\text{OH}$	21,010	0.10	2.21	22.1
(7)	$\beta\text{-C}_1\text{H}_2\text{ONa} + \text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	19,840	0.11	2.21	20.1
(7)	$\beta\text{-C}_1\text{H}_2\text{ONa} + \text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{OH}$	21,300	0.40	2.21	5.5
(8)	$\text{CH}_3\text{ONa} + \alpha\text{-C}_2\text{H}_5(\text{NO}_2)_2$	$\text{CH}_3\text{OH}$	20,590	6.11	2.48	0.4
(8)	$\text{C}_2\text{H}_5\text{ONa} + \alpha\text{-C}_2\text{H}_5(\text{NO}_2)_2$	$\text{C}_2\text{H}_5\text{OH}$	20,480	8.03	2.45	0.8
(9)	$(\text{CH}_3)_2\text{SO}_4 + \text{NaCN}$	$\text{CH}_3\text{OH}$	17,360	0.19	1.91	10.0
(9)	$(\text{CH}_3)_2\text{SO}_4 + \text{KCNS}$	$\text{CH}_3\text{OH}$	17,880	0.57	1.91	3.4
(10)	$(\text{C}_2\text{H}_5)_2\text{S} + \text{C}_2\text{H}_5\text{Br}$	$\text{C}_2\text{H}_5\text{CH}_3\text{OH}$	25,470	1.40	2.62	1.87
(11)	$\text{C}_2\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{OOCCH}_2\text{COOCCH}_3$	$\text{C}_2\text{H}_5\text{OH}$	16,760	0.17	1.80	10.6
(12)	$\text{NH}_4\text{CNO} \rightarrow (\text{NH}_4)_2\text{CO}$	$\text{H}_2\text{O}$	23,170	42.70	4.05	0.1
(13)	$\text{CH}_3\text{Cl}. \text{COOH} + \text{OH}^-$	$\text{H}_2\text{O}$	25,850	4.55	2.86	0.6
(14)	$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCOO}^-$	$\text{H}_2\text{O}$	9,060	0.15	3.52	0.04
(15)	$\text{CH}_3\text{I}. \text{COO}^- + \text{OH}^-$	$\text{H}_2\text{O}$	22,370	6.30	2.98	0.5
(15)	$\text{CH}_3\text{I}. \text{COO}^- + \text{C}_2\text{H}_5\text{O}^-$	$\text{H}_2\text{O}$	21,010	0.40	1.83	4.6
(15)	$\text{CH}_3\text{I}. \text{COOH} + \text{Cl}^-$	$\text{H}_2\text{O}$	22,850	7.90	2.66	0.3
(15)	$\text{CH}_3\text{Cl}. \text{COOH} + \text{I}^-$	$\text{H}_2\text{O}$	19,770	0.13	1.47	11.3
(15)	$\text{CH}_3\text{I}. \text{COOH} + \text{SCN}^-$	$\text{H}_2\text{O}$	18,190	0.40	2.17	5.4
(16)	$\text{CH}_3\text{OH}. \text{CH}_3\text{Cl} + \text{OH}^-$	$\text{H}_2\text{O}$	19,870	25.50	2.78	0.1
(17)	$\text{CH}_3[\text{CH}_2]\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	23,500	2.24	1.64	0.7
(17)	$\text{C}_2\text{H}_5\text{CO}[\text{CH}_2]\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	22,160	10.50	1.88	0.2
(18)	$\text{CH}_3[\text{CH}_2]\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	20,740	0.085	1.57	18.5
(18)	$\alpha\{\text{C}_2\text{H}_5\text{O}[\text{CH}_2]\text{Cl} + \text{I}^-\}$	$(\text{CH}_3)_2\text{CO}$	22,420	0.15	1.73	11.5
(19)	$\text{C}_2\text{H}_5\text{Br} + \text{OH}^-$	$\text{C}_2\text{H}_5\text{OH}$	21,400	4.30	3.86	0.9
(20)	$\text{C}_2\text{H}_5\text{Br}_2 + \text{I}^-$	$\text{C}_2\text{H}_5\text{OH}$	25,100	1.07	1.39	1.3

- (1) Talen, *Thesis*, Leiden (1927); *Tables Annuelles*, (1931).
- (2) Conrad, *Z. physikal. Chem.*, **3**, 350, (1889).
- (3) Hecht, Conrad, and Brückner, *ibid.*, **4**, 273, (1889).
- (4) Segaller, *Trans. Chem. Soc.*, **105**, 106, (1914).
- (5) Haywood, *ibid.*, **121**, 1904, (1922).
- (6) Conrad and Brückner, *Z. physikal. Chem.*, **7**, 274, (1891).
- (7) Cox, *Trans. Chem. Soc.*, **119**, 142, (1921).
- (8) Steger, *Z. physikal. Chem.*, **49**, 329, (1904).
- (9) Walden and Centnerzwer, *Z. Elektrochem.*, **15**, 310, (1909).
- (10) Corran, *Trans. Faraday Soc.*, **23**, 605, (1927).
- (11) Conrad and Brückner, *Z. physikal. Chem.*, **7**, 283, (1891).
- (12) Walker and Hambly, *Trans. Chem. Soc.*, **67**, 746, (1895).
- (13) Schwab, *loc. cit.*
- (14) Brinkman, Margaria, and Roughton, *Phil. Trans.*, **232**, 65, (1933).
- (15) Wagner, *Z. physikal. Chem.*, **115**, 121, (1925).
- (16) Evans, *ibid.*, **7**, 387, (1891).
- (17) Conant and Kirner, *J. Amer. Chem. Soc.*, **46**, 232, (1924).
- (18) Kirner and Richter, *ibid.*, **51**, 3408, (1929).
- (19) Grant and Hinshelwood, *Trans. Chem. Soc.*, **258**, (1933).
- (20) Dillon, *J. Amer. Chem. Soc.*, **54**, 952, (1932).

work† that  $E_A$  cannot be reproduced with an accuracy greater than  $\pm 1,100$  calories.‡

The reactions listed in Table I have normal velocities in the sense that the ratio of the empirical constant,  $A$ , to the calculated collision frequency does not differ appreciably from unity. It is customary to denote the inverse ratio by the letter  $P$ . Thus

$$P = A/Z. \quad (4)$$

Predominantly, these are reactions between ions and polar molecules. Due to the intensive work which has followed such a simple interpretation of the facts, several sets of somewhat similar data could now be added. It is not to be overlooked, however, that in this category there appear also some chemical changes between two ions and between two unionized molecules. In dealing with catalytic coefficients (Chapter X), moreover, we shall see that these essentially bimolecular constants can often be understood in the same way, whether the catalyst is an ion or an undissociated molecule.

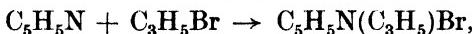
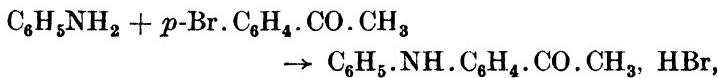
Prominent among chemical changes for which  $P$  has small values are the reactions of amines with halides, such as the union of triethylamine with ethyl iodide,



first investigated kinetically by Menschutkin.§ Norrish and Smith|| after an investigation of the reactions between trimethylamine and *o*- and *p*-nitrobenzyl-chloride in benzene solution,



and a review of the results of Cox†† and of Hawkins‡‡ upon the kinetics of two similar reactions in various solvents,



concluded that the ratio  $P$  was greater in polar solvents than in

† Tasman, *Snelheidsmetingen bij Ringopening van Phthaliederivaten*, Leiden, (1927).

‡ I am indebted to Dr. R. O. Gibson for procuring a copy of Dr. Tasman's work. He has also kindly pointed out that Hecht, Conrad, and Brückner's data on the interaction of methyl iodide and sodium ethoxide give, by the method of least squares, the constants  $A = 2.35 \times 10^{11}$  and  $E_A = 20,980$ . These values are more reliable than those given in the original table and retained here, and, incidentally, bring the ratio in the last column nearer to unity.

§ *Z. physikal. Chem.*, **6**, 41, (1890).

|| *Trans. Chem. Soc.*, **129**, (1928).

†† *Ibid.*, **119**, **142**, (1921).

‡‡ *Ibid.*, **121**, 1170 (1922).

non-polar solvents. Further results are given in Table 2, which is based on the work of Hawkins,<sup>†</sup> Hemptinne and Bekaert,<sup>‡</sup> Essex and Gelormini,<sup>§</sup> Byrne,<sup>||</sup> and Preston and Jones.<sup>††</sup> A slightly inaccurate collision formula has been used in calculating the theoretical

*Table 2*  
*Reactions with Velocities less than those predicted by the Simple Collision Theory*

Reaction	Solvent	$E_A$	$k_{\text{at}^{\circ}\text{C.}}$		$\frac{k_{\text{calculated}}}{k_{\text{observed}}}$
			Observed $\times 10^5$	Calculated $\times 10^{-2}$	
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N + C <sub>2</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>6</sub>	11,190	1.28	239	$1.9 \times 10^9$
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> + CH <sub>3</sub> I	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	11,680	45.4	93.1	$2.1 \times 10^7$
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N + C <sub>2</sub> H <sub>5</sub> Br	(CH <sub>3</sub> ) <sub>2</sub> CO	11,710	17.5	108	$6.2 \times 10^7$
p-H $\phi$ NH <sub>2</sub> + H $\phi$ Cl <sup>†</sup>	99.6% C <sub>2</sub> H <sub>5</sub> OH	11,860	9.80	36.1	$3.7 \times 10^7$
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N + C <sub>2</sub> H <sub>5</sub> Br	{ 50% (CH <sub>3</sub> ) <sub>2</sub> CO 50% C <sub>6</sub> H <sub>6</sub> }	12,040	8.97	65.5	$7.3 \times 10^7$
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N + C <sub>2</sub> H <sub>5</sub> Br	{ 80% (CH <sub>3</sub> ) <sub>2</sub> CO 20% C <sub>6</sub> H <sub>6</sub> }	12,100	16.0	59.7	$3.7 \times 10^7$
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N + C <sub>2</sub> H <sub>5</sub> Br	{ 20% (CH <sub>3</sub> ) <sub>2</sub> CO 80% C <sub>6</sub> H <sub>6</sub> }	12,180	4.92	53.0	$1.1 \times 10^8$
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> + CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	13,020	6.65	12.4	$1.9 \times 10^7$
C <sub>6</sub> H <sub>5</sub> N + CH <sub>3</sub> I	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	13,220	182	9.04	$5.0 \times 10^6$
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> + H $\phi$ Cl	99.6% C <sub>2</sub> H <sub>5</sub> OH	13,450	13.8	3.25	$2.4 \times 10^6$
CS(NH <sub>2</sub> ) <sub>2</sub> + CH <sub>3</sub> I	(CH <sub>3</sub> ) <sub>2</sub> CO	13,620	383	4.45	$1.2 \times 10^6$
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> I	(CH <sub>3</sub> ) <sub>2</sub> CO	13,680	3.11	4.81	$1.6 \times 10^7$
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> + CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	14,400	250	1.50	$6.0 \times 10^6$
(S(NH <sub>2</sub> ) <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> I	C <sub>2</sub> H <sub>5</sub> OH	14,620	143	0.973	$6.8 \times 10^6$
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> + p-NO <sub>2</sub> Cl	99.6% C <sub>2</sub> H <sub>5</sub> OH	14,680	5.77	0.548	$9.5 \times 10^6$
(CH <sub>3</sub> ) <sub>2</sub> NH + C <sub>3</sub> H <sub>6</sub> I	C <sub>2</sub> H <sub>5</sub> OH	14,740	275	1.10	$4.0 \times 10^6$
(iso-C <sub>5</sub> H <sub>11</sub> ) <sub>3</sub> N + C <sub>3</sub> H <sub>6</sub> I	C <sub>2</sub> H <sub>5</sub> OH	15,190	180	0.577	$3.2 \times 10^6$
p-H $\phi$ NH <sub>2</sub> + H $\phi$ Cl	99.6% C <sub>2</sub> H <sub>5</sub> OH	16,050	25.2	0.063	$2.5 \times 10^4$

<sup>†</sup>  $\phi = -C_6H_4CH_2-$  or  $-CH_2C_6H_4-$ .

rates,<sup>††</sup> but this is now of no consequence. Considering the results broadly, it is seen that rates which for normal reactions would be associated with an energy of activation of about 22,000 calories are here related to reactions which in all cases have values well below that figure. Furthermore, the divergence between the experimental and theoretical  $k$ 's diminishes steadily as the observed value of  $E$  increases, finally disappearing as  $E$  approaches that quantity (22,000

<sup>†</sup> Loc. cit.

<sup>‡</sup> Z. physikal. Chem., **28**, 225, (1899).

<sup>§</sup> J. Amer. Chem. Soc., **48**, 882, (1926).

<sup>||</sup> Thesis, Liverpool, (1924).

<sup>††</sup> Trans. Chem. Soc., **101**, 1930, (1912).

<sup>‡‡</sup> Moolwyn-Hughes, Chemical Reviews, **10**, 241, (1932).

calories) which characterizes normal reactions proceeding with this rate. The observed critical increments may thus be false, in the sense that—by some unknown mechanism—they have been depressed from the normal values. It may also be significant that these reactions, and others in the same category, are highly exothermic, the heat evolved being not very different from the energy of activation:

Reaction	Solvent	<i>E</i>	<i>Q</i>
$(\text{CH}_3)_3\text{NC}_3\text{H}_5 + \text{CH}_3\text{I}$	$\text{C}_6\text{H}_5\text{NO}_2$	13,020	15,000†
$(\text{CH}_3\text{CO})_3\text{O} + \text{H}_2\text{O}$	$\text{H}_2\text{O}$	10,600‡	9,400§

† Essex and Gelormini, *J. Amer. Chem. Soc.*, **48**, 882, (1926).

‡ Verkade, *Rec. trav. chim. Pays-bas*, **33**, 299, (1915).

§ Thomsen, *Thermochemistry*, p. 373, (1908).

The catalytic hydrolyses of the glycosides typify reactions of a bimolecular character, the rates of which generally exceed those anticipated if the assumptions underlying equation (1) are valid. The catalytic coefficients are the unimolecular velocity constants divided by the activity of the hydrogen ion, measured electrometrically, which, at infinite dilution, is identical with the concentration of ionic catalyst. Some experimental results† are summarized in

*Table 3*  
*Reactions with Velocities greater than those predicted by the Simple Collision Theory*

Glycoside	$k_{\text{H}^+}$ at 60° C.	<i>E<sub>A</sub></i>	$\ln_e A$	$E_A/\ln_e A$	$\frac{k_{\text{calculated}}}{k_{\text{observed}}}$
Trehalose	$8.64 \times 10^{-7}$	40,180	46.98	855	$1.10 \times 10^{-9}$
Melibiose	$1.55 \times 10^{-5}$	38,590	47.46	813	$6.82 \times 10^{-10}$
$\beta$ -Methyl-glucoside	$3.86 \times 10^{-6}$	33,730	38.69	872	$4.40 \times 10^{-6}$
Gentiobiose	$1.24 \times 10^{-6}$	33,390	37.02	902	$2.32 \times 10^{-5}$
Turanose	$1.19 \times 10^{-6}$	32,450	37.87	857	$9.89 \times 10^{-6}$
Salicin	$1.80 \times 10^{-5}$	31,630	37.05	854	$2.26 \times 10^{-5}$
Maltose	$1.68 \times 10^{-5}$	30,970	35.99	859	$6.52 \times 10^{-5}$
Arbutin	$4.34 \times 10^{-5}$	30,760	36.62	840	$3.52 \times 10^{-5}$
Celllobiose	$5.89 \times 10^{-6}$	30,710	36.81	834	$3.65 \times 10^{-5}$
Sucrose	$1.46 \times 10^{-2}$	25,830	34.93	738	$1.88 \times 10^{-4}$
Melezitose	$4.83 \times 10^{-3}$	25,600	33.49	764	$7.94 \times 10^{-4}$
Raffinose	$1.12 \times 10^{-2}$	25,340	33.96	746	$4.95 \times 10^{-4}$
Lactose	$1.66 \times 10^{-5}$	24,680	26.51	931	$8.54 \times 10^{-1}$

Table 3, from which it is seen that, with the exception of the apparently fortuitous case of lactose, the velocity of reaction is greater than that

† Moelwyn-Hughes, *Trans. Faraday Soc.*, **24**, 309, (1928); *ibid.*, **25**, 81, 503, (1929).

expected by a factor which amounts to  $10^6$  for trehalose. We also note that  $E_A/\ln_e A$  is approximately constant for reactions of a given type, having different values for glucosides, fructosides, and galactosides. This is a purely empirical observation though not without interest, and resembling other empirical relationships to be discussed later (p. 294).

We have now seen that there are reactions in solution with rates greater than, about equal to, and less than the rates computed on the assumption that chemical change takes place whenever two molecules meet with an energy of  $E$  or more, and when the energy is such that it can be accommodated in two square terms. In other words,  $P$  can exceed, be equal to, or be less than unity. It has become customary to refer to such reactions as slow, normal, and fast; the adjectives have no relation, of course, to the absolute velocity of reaction. It is now a matter of interest to discover how the chemical changes which have been investigated distribute themselves among these three rather arbitrary categories. A method used by Polanyi and Wigner† was employed on the data for the 181 bimolecular reactions then to hand.

In Fig. 1 the abscissae are values of  $\log_{10} A$ , determined experimentally from the Arrhenius curves, and the ordinates give the number of reactions with the assigned value of  $A$ . Whereas 35 reactions have values of  $A$  lying between  $10^{11}$  and  $10^{12}$ , only 6 have values 100 times greater. The maximum probability refers to  $\log_{10} A = 11.3$ , which is in very striking proximity to the theoretical collision frequency for all the systems involved. In other words, more bimolecular reactions belong to the normal group than to any other. Since the slope of the curve is steeper on the high side of  $A$ , it is evident that fast reactions are of less frequent occurrence than slow ones.

Chief among the causes responsible for reducing below its normal value the rate of a second-order reaction in a homogeneous system are: (1) endothermic formation of a complex prior to the reaction proper; (2) the necessity for the ionization of either or both of the reactants; (3) deactivation by solvent molecules; (4) stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact, and (5) the existence of strong forces of repulsion. Factors which allow a faster reaction velocity than that

† *Z. physikal. Chem., Haber-Band*, 439, (1928).

permitted by the simple collision theory are: (a) exothermic formation of a complex prior to the reaction proper; (b) the distribution of the energy of activation among a number of internal degrees of freedom of the reacting molecules; (c) the propagation of reaction chains; (d) activation by some means other than by collision, e.g. by

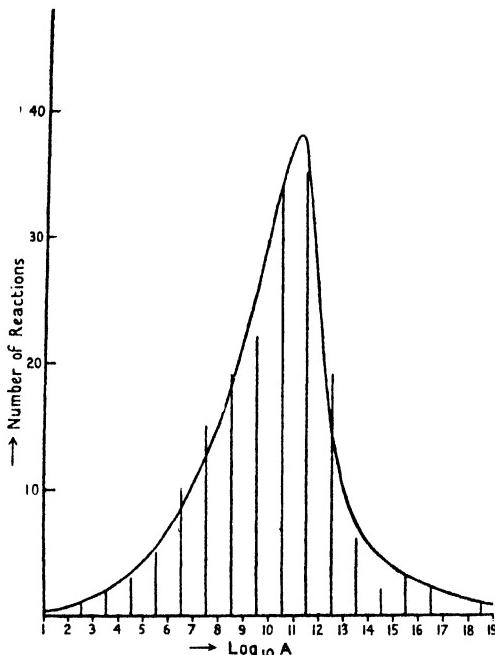


FIG. 1.

radiation, and (e) the existence of strong forces of attraction. Evidence from individual reactions could be quoted in support of each of these.

The following must serve as provisional clues for detecting the factors likely to be at work. Activation due to radiation is most readily demonstrated by investigating the reaction in the dark† and in the presence of suitable illumination. The presence of reaction chains is to be suspected in all cases where the instantaneous velocity ( $dc/dt$ ) is either a function of the initial concentration raised to a high power,

† When a reaction is suspected of being catalysed by visible light, the dark reaction may be studied in a thermostat containing a liquid which is deeply coloured. Nigrosin is a useful dye for water-thermostats. Alternatively, the reaction vessel may be painted black, or kept in a metal container. Solutions may be prepared in a room flooded with light of least injurious colour.

or is sensitive to the presence of added substances. Ionization may be expected to enter into the problem, particularly with solvents of high dielectric capacity, whenever the rate of chemical change varies markedly with the dilution, and with the addition of electrolytes. When the apparent energy of activation undergoes a profound change from solvent to solvent, the formation of a complex is indicated.

Photo-activation and the propagation of reaction chains usually go hand in hand, but are not of frequent occurrence. There thus remain three possible methods of explaining the velocity of fast reactions. Activation among a number of degrees of freedom is always possible theoretically with polyatomic molecules. If the maximum value of  $F$  allowable does not account for the rate, we must have recourse to the alternative ideas (*a*) and (*e*).

In view of the experimental evidence that deactivations do not occur in those reactions where the hypothesis has been put to the test (p. 242), this explanation of slow reactions must be regarded as being less probable than the other suppositions.

### *Critique*

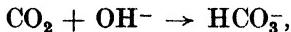
The foregoing analysis has been based on equation I(21), which is a valid formula for the frequency of collisions between spherical molecules of incompressible radii which exert no forces on one another and are uninfluenced by the presence of other molecules. The actual systems considered are those in which reaction takes place between molecules which are not spherical, are certainly compressible, exert powerful forces on one another, and are greatly influenced by their molecular neighbours. Anything approaching exact agreement would be, under the circumstances, a matter for surprise. The question which must be decided, however, is not whether close numerical agreement ensues from the application of the simple collision theory, but whether the collision equation is right with regard to order of magnitude and with regard to its dependence on molecular weight and, particularly, on temperature. It will be easier to provide the answer at a later stage. One may at this juncture, however, ponder whether the advances made in the kinetics of reactions in solution during the last fifteen years would have been possible had the collision theory, on which they are based, been fundamentally at fault.

La Mer concludes† that the collision theory, as applied by Hinshel-

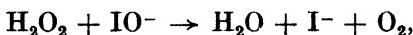
† *J. Chem. Physics*, 1, 289, (1933).

wood and Moelwyn-Hughes to bimolecular reactions in gases and in solution, is valid only under conditions which appear to him to be improbable from quantal, thermodynamic, and experimental angles.

Polissar<sup>†</sup> and others<sup>‡</sup> have raised the interesting point that agreement with the collision theory may be a consequence of the restricted range of velocities accessible to direct measurement. There are many ways of countering this charge. The most direct is to recall reactions which, though having inconveniently rapid velocities, are still in agreement with theory. One such is the formation of the bicarbonate ion,<sup>§</sup>



which has been carefully investigated on account of its physiological importance. When we interpret the results in terms of the collision theory, there nevertheless emerges quite a reasonable value for the sum of the radii of the hydroxyl ion and the carbon dioxide molecule. The conversion of the blue ion (*p*-NO<sub>2</sub>. C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C<sup>+</sup> into the corresponding methane is catalysed by undissociated molecules of monochloracetic acid, but the rate is very rapid under ordinary conditions. At -60° C., in a mixed solvent (85 per cent. C<sub>2</sub>H<sub>5</sub>OH; 15 per cent. C<sub>6</sub>H<sub>5</sub>. CH<sub>3</sub>), it is slow enough to be followed, and the experimental value of *A* (8.65 × 10<sup>11</sup> litres/gram mole-second) shows an agreement with the prediction of the simple collision theory which is as reasonable as it was apparently unexpected.<sup>||</sup> The bimolecular velocity coefficient for the reaction between hydrogen peroxide and the hypoiodous ion in water,



at 25° C. is 2 × 10<sup>11</sup> litres/gram molecule-second, which, as the investigator has pointed out,<sup>††</sup> is consistent with the occurrence of chemical change at each collision. Two things can be said of these very diverse reactions, the rates of which at 25° C. differ by a factor of 7 × 10<sup>6</sup>. (1) They are all inconveniently rapid at room temperatures. The first one was examined by the Hartridge-Roughton photoelectric method; the second by lowering the temperature by 85°; and the third by indirect means. (2) They are all in reasonable agreement with equation (1).

<sup>†</sup> *J. Amer. Chem. Soc.*, **54**, 3105, (1932).

<sup>‡</sup> e.g. D. T. Lewis and Huddleston, *Trans. Chem. Soc.*, 1398, (1932); Ogg and O. K. Rice, *J. Chem. Physics.*, **5**, 140, (1937).

<sup>§</sup> Brinkman, Margaria, and Roughton, *loc. cit.*

<sup>||</sup> G. N. Lewis and G. T. Seaborg, *J. Amer. Chem. Soc.*, **61**, 1894, (1939).

<sup>††</sup> Liebhafsky, *ibid.*, **54**, 1792, 3499, (1932).

Had a collision equation other than the ideal gas one been employed as a basis of calculation, we should, of course, have still found a division of reactions into normal, slow, and fast ones, but the standard of normality might have been different. Many alternative collision formulae, discussed in Chapter VIII, have, in fact, been applied to some of the data discussed here. The chief criticism one can level at such applications is the failure to apply them to the gross and scope of our experimental material, rather than any inherent invalidity of the equations.

We shall see later (Appendix II) that exact collision formulae can be developed for certain simple systems, such as reactions involving three or four atoms, in the gaseous phase, and that equations of the correct form can also be worked out for simple reactions in solution. To adopt them now would only give us the dubious benefit of replacing the single parameter  $(r_A + r_B)$ , of which we admittedly know little, by a number of other parameters, such as valency angles, interatomic frequencies, and torsional coefficients, of which we know still less.

### *The Kinetics of Analytical Reactions*

Because we say of the reactions of analytical chemistry that they are instantaneous, when we mean that they are too rapid for us to measure by the usual devices, we should be on our guard against drawing the conclusion that no energy of activation is necessary.

An analytical reaction which, with decinormal reagents at 18° C., is over to the extent of 99.9 per cent. in one-tenth of a second would justifiably be called a quick reaction and an analytically suitable one. If the change is bimolecular, however, we would expect  $k_2$  to have the order of magnitude  $10^5$  litres/gram mole-second, according to equation II(4), and therefore an activation energy of 8,600 calories, according to equation (1). The value found for the decolorization of starch-iodine by thiosulphate is, in fact, about 8,000 calories.†

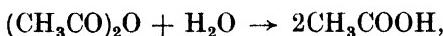
### *The Role of Electrostatic Effects in the Kinetics of Bimolecular Reactions*

Most of the reactions for which  $P$  is about unity take place between ions and polar molecules, and most of the reactions for which  $P$  is much less than unity take place between two polar molecules.‡ The

† von Halban and Eisner, *Helv. Chim. Acta*, 19, 915, (1936).

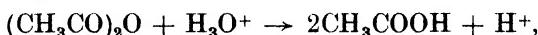
‡ Moelwyn-Hughes, *Dissertation*, Oxford, (1932); Grant and Hinshelwood, *Trans. Chem. Soc.*, 258, (1933).

contrast is the more striking when we examine the rates of the reactions of a molecule with both an ion and another molecule. The bimolecular velocity coefficient for the hydration of acetic anhydride in acetone solution,



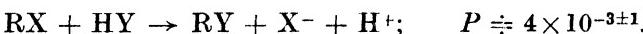
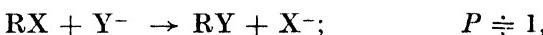
is approximately†  $k = 10^5 \times e^{-16000/RT}$ ,

indicating that  $P$  is about  $3 \times 10^{-7}$ . The catalytic coefficient for the hydration in aqueous acidic solution,



is approximately‡  $k = 3.6 \times 10^{10} \times e^{-17280/RT}$ ,

which points to a value of approximately 1 for  $P$ . Similarly, when we examine an ion-dipole reaction with the corresponding dipole-dipole reaction in the same solvent, we have, as rough values:§



Here  $R$  is an alkyl or aryl group, and  $Y^-$  stands for  $R'O^-$  or the hydroxyl ion.

It would thus appear that an electrostatic field is helpful if not necessary for transformations undergone by molecules in solution, and that it can be suitably furnished by the presence of ions. There is some truth in the contention, but we must not limit our vision to hydroxylic solvents. The iodine atom attacks the ethylene iodide molecule in carbon tetrachloride solution at just the rate which we would expect on the basis of the collision theory.|| Here we have a system from which electrostatic effects have been as far as possible removed, and similar systems will be discussed later. But though, by choosing solvents of low dielectric capacity and reactants of low or zero polarity, we may eliminate electrostatic effects, we can never eliminate the ever-present forces of other origins. The principle under discussion should therefore be reformulated in broader terms. All atoms, molecules, and ions exert upon one another forces of attraction and repulsion which increase in magnitude as the distance between them gets less. Bimolecular chemical changes always require the proximity of one atom, ion, or molecule to another, and

† Philip, *Trans. Chem. Soc.*, **28**, 259, (1912).

‡ Computed from the data of Jowett, *Dissertation*, Liverpool, (1923).

§ Moelwyn-Hughes, *Acta Physicochimica, U.S.S.R.*, **4**, 173, (1936).

|| Polissar, *J. Amer. Chem. Soc.*, **52**, 956, (1930).

are therefore associated with stronger forces than are at work in systems at equilibrium. Chemical change in all states of matter must therefore be closely linked with the nature of the forces at work. These may sometimes be the exchange forces of quantal mechanics, sometimes the electrostatic forces of classical mechanics, and sometimes both. To recognize the type of forces which are effective in the wide variety of changes, the rates of which are measurable, now constitutes an important part of chemical kinetics.

The subject-matter in the four chapters which follow has been divided on the basis of the type of force at work, as this seems to be, primarily, the origin of their kinetic characteristics.

### *Modifications in the Scope of the Subject-matter*

The scheme of this work differs from that of the first edition in other respects. Certain matters which could be dismissed in a paragraph in 1933 now require a full chapter. Other matters, dealt with at some length in the first edition, are hurriedly passed over—not because their importance has lessened, but because they have since been made the subject of separate monographs. The reader is especially advised to consult the cognate works selected in this list:

- Orthohydrogen, Parahydrogen and Heavy Hydrogen*, A. Farkas: Cambridge, (1935).
- Chemical Kinetics and Chain Reactions*, Semenoff: Oxford, (1935).
- Physical Aspects of Organic Chemistry*, Waters: Routledge, (1935).
- Polymerisation*, R. E. Burk, H. E. Thompson, A. J. Weith, and Ira Williams: Reinhold, New York, (1937).
- Diffusion und chemische Reaktion in festen Stoffen*, Jost: Steinkopff, Dresden and Leipzig, (1937).
- Catalysis from the Standpoint of Chemical Kinetics*, G.-M. Schwab, translated by H. S. Taylor and R. Spence: Macmillan, (1937).
- Chemische Gasreaktionen*, Schumacher: Steinkopff, Dresden and Leipzig, (1938).
- Chemical Kinetics*, J. Farringdon Daniels: Cornell, (1938).
- The Theory of Rate Processes*, Glasstone, Laidler, and Eyring: McGraw-Hill Book Co., New York, (1941).
- Physical Organic Chemistry*, Hammett: McGraw-Hill Book Co., (1940).
- Acid-Base Catalysis*, Bell: Oxford, (1941).
- Modern Theories of Organic Chemistry*, Watson: Oxford, (1941).
- Recent Work in the Field of High Pressures*, P. W. Bridgman: *Reviews of Modern Physics*, (1946).

### *Intermolecular Forces in Chemical Kinetics*

Two examples have already been given of the application of interatomic forces to kinetic problems. The first was the application of the valency force theory to determine the energy of activation of triatomic reactions in the gaseous state (p. 14), and the second referred to the effect of repulsive forces on the frequency of collisions between molecules of solute and solvent (p. 12). The derivation of the gas collision formula implies the existence of an artificial and discontinuous force field, which is zero when the distance apart of the centres of the colliding molecules exceeds ( $r_A + r_B$ ) and is infinite when the distance apart is less than this amount. We must now briefly discuss other types of forces† and their general application to the problem of the velocity of chemical change.‡

It will prove more convenient to deal with the intermolecular energy,  $u$ , than with the intermolecular force,  $X$ , to which it is related, in terms of the separation,  $r$ , as follows

$$X = -\frac{du}{dr}. \quad (5)$$

1. *The Energy of Interaction of two Atoms.* Atoms held together by a covalent link repel each other with an energy  $D_e e^{-2a(r-r_e)}$  and attract each other with an energy  $-2D_e e^{-a(r-r_e)}$ , where  $D_e$  is the energy of dissociation of the link,  $r_e$  the equilibrium separation, and  $a$  an empirical constant.§ The total interaction energy is thus

$$u = D_e \{e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}\}. \quad (6)$$

This equation was used|| in the first evaluation of an activation energy (p. 15). Many other reactions in the gaseous phase have been treated in a similar fashion.††

2. *The Energy of Interaction of two Ions.* According to the well-known laws of Coulomb and Faraday, the energy of interaction of

† See Lennard-Jones, Chapter X in Fowler's *Statistical Mechanics*, 2nd ed., Cambridge, (1938); London, *Trans. Faraday Soc.*, 33, 1, (1936); J. Sherman, *Chem. Rev.*, 11, 93, (1933); Lennard-Jones and A. Sherman, *Reports of the London Physical Society*, (1935); Moelwyn-Hughes, *Physical Chemistry*, Cambridge, (1940).

‡ Ingold, *Trans. Chem. Soc.*, 1032, (1930); Waters, *ibid.*, 1551, (1933); Moelwyn-Hughes and A. Sherman, *ibid.*, 101, (1936).

§ Morse, *Phys. Rev.*, 34, 57, (1929).

|| Eyring and Polanyi, *Z. physikal. Chem.*, B, 12, 279, (1931).

†† Eyring, A. Sherman, and Kimball, *J. Chem. Physics*, 1, 586 (1933); Gershinowitz and Eyring, *J. Amer. Chem. Soc.*, 57, 985, (1935); M. G. Evans and Polanyi, *Trans. Faraday Soc.*, 34, 11, (1938); M. G. Evans and Warhurst, *ibid.*, 34, 614, (1938).

an ion of charge  $z_A \epsilon$  and another ion of charge  $z_B \epsilon$  at a distance  $r$  apart in a medium of dielectric constant  $D$  is

$$u = \frac{z_A z_B \epsilon^2}{Dr}. \quad (7)$$

In this equation,  $\epsilon$  stands for the magnitude of the electronic charge ( $4.77 \times 10^{-10}$  e.s.u.), and  $z$  for the electrovalency. Thus we would write  $z_A = +1$  for the sodium ion and  $z_B = -2$  for the sulphate ion. Clearly, the interionic force may be one of repulsion or attraction, according to the similarity or dissimilarity of the signs of the charges.  $D$  is unity for a vacuum, is often about 2 for non-polar liquids, and may be as great as 80 for hydroxylic solvents. The interionic energy is therefore always less in solution than in the gaseous phase.

The first successful application of this equation to the kinetics of reactions in solution is due to Ingold,<sup>†</sup> who applied it to explain the relative velocities of esterification of the mono-alkyl esters of certain dicarboxylic acids. His method is applicable to the study of the relative rates of all reactions between a common ion on the one hand, and a molecule with or without an electrical charge on the other hand. Thus, for example, it is found that *N*-acetylmethylglucosaminide,  $\alpha$ -methylglucoside, and  $\beta$ -methylglucoside are hydrolysed in the presence of *N*-hydrochloric acid at 80° C. at rates which are, respectively, 350, 100, and 180 times faster than the rate of hydrolysis of the hydrochloride of methylglucosaminide. The slowness of the last reaction is due to the repulsion exerted by the charged amino group, in the  $\alpha$ -position to the carbon atom attacked, on the hydrogen ion, so that, since we are dealing with univalent charges, the relative rates are

$$k/k_0 = e^{-\epsilon^2/DrkT}. \quad (8)$$

In order to explain the observed ratios, a value of  $r = (1.5 \pm 0.2) \times 10^{-8}$  cm. is required,<sup>‡</sup> which is not an unreasonable figure in view of the uncertainty as to the exact value of  $D$  to employ. Very simple electrostatic principles thus suffice to explain the relative rates of comparable reactions, though the precise mechanism of either may remain unsolved. It is, incidentally, interesting to note that, despite a greater experimental uncertainty than prevails for the hydrolysis of unsubstituted glycosides (p. 74), the data of Moggridge and

<sup>†</sup> *Trans. Chem. Soc.*, 1375, (1930).

<sup>‡</sup> Moggridge and Neuberger, *ibid.*, 745, (1938).

Neuberger indicate a value of about -71 calories per gram mole degree for  $dE_A/dT$  at 97.4° C.

The application of equation (7) to systems at equilibrium is due to Bjerrum,<sup>†</sup> in whose hands the problem of the effect of a resident charge on the dissociation constant of a dibasic organic acid has been partially solved.

Two ions in solution are not usually retained at an invariant distance,  $r$ , apart, but are subject to fluctuations, which on the average lead to a preponderance of ions of a given sign round an ion of opposite sign. The effect of the cloud of oppositely charged ions is to lower the interaction energy of a pair, by an amount which, as Debye and Hückel<sup>‡</sup> have shown, varies as the square root of the ionic strength. The introduction of this cloud contribution by Bjerrum<sup>§</sup> and Brönsted<sup>||</sup> has elucidated the effect of electrolytes on the velocity of reactions between ions at a constant temperature. Without introducing the environmental effect in this way, equation (7), applied directly to data extrapolated to infinite dilution, adequately accounts for  $P$  factors ranging from  $10^{-8}$  to  $10^{-8}$ , as is more fully described in the following chapter.

*3. The Energy of Interaction of an Ion and a Permanent Dipole.* By summing the two Coulombic terms which come into play when an ion, of charge  $z_A \epsilon$ , acts on a dipole of moment  $\mu_B$  and length  $l$ , it is readily shown that the energy of interaction is approximately

$$u = \frac{z_A \epsilon \mu_B \cos \theta}{r^2} \left(1 - \frac{3l^2}{8r^2}\right), \quad (9)$$

where  $\theta$  is the angle of inclination of the polar axis to the line joining its centre to that of the ion (Fig. 2). When the distance,  $l$ , between the two poles is small compared with the distance,  $r$ , between the ion and the dipole, we obtain

$$u = \frac{z_A \epsilon \mu_B \cos \theta}{r^2}. \quad (10)$$

Here again, the force exerted may be one of repulsion or of attraction, depending on the angle  $\theta$ . The position of minimum energy, which is the one to which the system tends, is one of attraction, with  $\theta = 0$  when  $z_A$  is negative.

<sup>†</sup> *Z. physikal. Chem.*, **106**, 219, (1923).

<sup>‡</sup> *Physikal. Z.*, **25**, 97, (1924).

<sup>§</sup> *Z. physikal. Chem.*, **118**, 251, (1925).

<sup>||</sup> *Ibid.*, **115**, 337, (1925).

A relatively early attempt to correlate the rates of chemical reactions with the magnitude of the electrical moments of substituted groups was made by Waters,<sup>†</sup> whose work has been further developed by Spong<sup>‡</sup> and by Moelwyn-Hughes.<sup>§</sup>

Ingold and his collaborators<sup>||</sup> have also put equation (10) to good

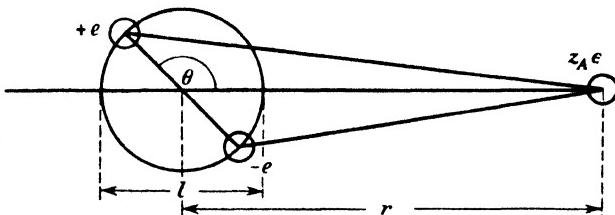
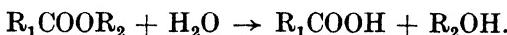


FIG. 2. The interaction of an ion and a permanent dipole.

use in separating the effect of permanent molecular polarity from the steric and other influences which are at work in the hydrolysis of aliphatic esters:



The rates of hydrolysis by acids have long been known to be sensitive to substitution of a  $\text{CH}_2$  group into  $\text{R}_1$  but not into  $\text{R}_2$ , as shown in Table 4.<sup>††</sup>

Table 4

	$k_{45^\circ}\text{c.} \times 10^3$		
	Acetate	Propionate	Butyrate
Methyl	6.6	7.1	3.9
Ethyl	6.8	7.3	4.2
Propyl	6.7	7.2	4.1

When the same esters are hydrolysed by alkalis, neither  $\text{R}_1$  nor  $\text{R}_2$  can be modified without causing a noticeable change in the velocity. If, however, the dipole moment of the ester comes into the picture, it should exert an effect which depends on the sign of the attacking ion. Ingold<sup>††</sup> accordingly focused attention on the ratio,  $k_{\text{OH}^-}/k_{\text{H}^+}$ , of the rate of hydrolysis of a given ester by hydroxyl ions and the rate of hydrolysis of the same ester by hydrogen ions, and found

<sup>†</sup> *Phil. Mag.*, 8, 436, (1929).

<sup>‡</sup> *Trans. Chem. Soc.*, 1283, (1934).

<sup>§</sup> *Proc. Roy. Soc.*, 157, 667, (1936).

<sup>||</sup> Burton and Ingold, *Trans. Chem. Soc.*, 904, (1924); Ingold, Jackson, and Kelly, *ibid.*, 2035, (1931).

<sup>††</sup> van 't Hoff, *Studies in Chemical Dynamics*, p. 119, (1896).

<sup>‡‡</sup> *Trans. Chem. Soc.*, 1032, (1930).

the ratio to vary from one ester to another in the way expected from the sign and magnitude of the dipole moment of the radical substituted into  $R_1$  or  $R_2$ .

4. *The Energy of Interaction of two Permanent Dipoles.* Electrical dipoles, of moments  $\mu_A$  and  $\mu_B$ , attract and repel one another by the same laws as those which govern the interaction of magnetic dipoles. The sign and magnitude of the energy depend not only on the distance,  $r$ , apart of their centres but on the angles of inclination. Maximum interaction occurs when the dipoles are in the head-to-tail position in a straight line passing through the molecular axes, when, by adding the four Coulombic terms, it is found to be approximately

$$u = -\frac{2\mu_A \mu_B}{r^3(1-l^2/r^2)}. \quad (11)$$

When the distance,  $r$ , greatly exceeds the length,  $l$ , of the dipoles, this expression reduces to

$$u = -\frac{2\mu_A \mu_B}{r^3}. \quad (12)$$

This electrostatic energy influences chemical reactions between polar molecules, the kinetics of which have frequently been discussed.<sup>†</sup>

5. *Energies of Induction.* A symmetrical atom such as neon, or molecule such as methane, is usually non-polar. When subject to

an external electric field, the electrons and nuclei of the particle are partially displaced from their normal disposition, and the particle temporarily acquires a polar character. The distortion of the particle is due to the displacement of the nuclei and electrons, but the more mobile electrons are responsible for the chief effect, as is indicated schematically in Fig. 3. A particle initially non-polar

which temporarily acquires polarity is said to possess an induced—as distinct from a permanent—electrical moment. For fields of moderate strengths, the magnitude of the induced moment may reasonably be assumed to be directly proportional to the field strength  $F$ , hence:

$$\mu_i = \alpha F. \quad (13)$$

<sup>†</sup> e.g. Williams and Hinshelwood, *Trans. Chem. Soc.*, 1079, (1934); Moelwyn-Hughes and Sherman, *loc. cit.*; Moelwyn-Hughes, *Trans. Faraday Soc.*, 34, 98, (1938).

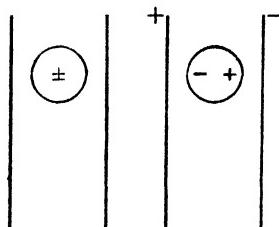


FIG. 3.

The proportionality constant  $\alpha$ , is termed the polarizability of the particle. The work done in inducing the moment is readily found. The force acting on unit charge, i.e. the field, is  $F$ , and the force acting on a charge  $e$  is  $Fe$ . The work expended in inducing the dipole is the product of this force and the distance through which the charge is drawn, hence:

$$w = \int_0^l Fe dl = \int_0^l \frac{\mu_i}{\alpha} e dl = e^2 \int_0^l \frac{l dl}{\alpha} = \frac{1}{2} \frac{e^2 l^2}{\alpha} = \frac{1}{2} \frac{\mu_i^2}{\alpha} = \frac{1}{2} \alpha F^2.$$

There are thus two equivalent expressions for the displacement energy of the induced dipole, viz.

$$w = u_i = \frac{1}{2} \frac{\mu_i^2}{\alpha} = \frac{1}{2} \alpha F^2. \quad (14)$$

The standard to which this potential energy refers is seen to be that of zero potential energy for the undisplaced (superimposed) charges.

Let us now consider again those molecules such as hydrogen bromide which have permanent dipole moments in the absence of an external field. We may conclude that the dipole is due to the internal field of the molecule, and, by analogy, ascribe to these also a potential energy  $u_i = \frac{1}{2} \mu^2 / \alpha$ , where  $\mu$  is the permanent dipole moment.

When an ion ( $A$ ), such as the iodide ion  $I^-$ , approaches a molecule ( $B$ ) which is normally non-polar, such as the iodine molecule  $I_2$ , the potential energy varies due to effects which may be conveniently regarded as if they were two processes. The field,  $F$ , set up by the ion of charge  $\epsilon$  (in magnitude, irrespective of sign) is  $F = \epsilon/r^2$ ; this induces in the molecule a moment  $\mu_B = \alpha_B F$ . Now the potential energy of the system due to the induction we have seen is

$$u_i = \frac{1}{2} \alpha F^2 = \frac{1}{2} \alpha_B \left( \frac{\epsilon}{r^2} \right)^2.$$

But the molecule now attracts the ions, exactly as if it possessed a permanent moment, and the energy of attraction of the ion-induced dipole system is, by equation (10),

$$u_a = -\frac{\epsilon \mu_B}{r^2} = -\frac{\epsilon}{r^2} \alpha_B F = -\alpha_B \left( \frac{\epsilon}{r^2} \right)^2.$$

Hence the total potential energy of the system is

$$u = u_i + u_a = -\frac{1}{2} \alpha_B \frac{\epsilon^2}{r^4} = -\frac{1}{2} \alpha_B F^2. \quad (15)$$

It is to be observed that the net effect is always negative, or, in other words, that the total electrostatic interaction of an ion and an induced dipole is one of attraction.

Consider two molecules *A* and *B* to be initially non-polar, but to be so constituted that when they approach each other they set up between them electrical fields which induce dipoles in both molecules. We know that the magnitude of the induced dipole is, in general,

$$\mu = \alpha F, \quad (13)$$

and that the potential energy of the dipole in a field of strength *F* is

$$u = -\frac{1}{2}\alpha F^2. \quad (15)$$

Now let the molecule *A* possess a dipole  $\mu_A$ , so that it exerts a field of strength

$$F_A = \frac{\mu_A}{r^3} \sqrt{(1 + 3 \cos^2 \theta_A)}.$$

This field induces a dipole in molecule *B*, which has polarizability  $\alpha_B$ . The energy of interaction due to the field of *A* acting on the induced dipole in *B* is

$$\begin{aligned} u_{A \rightarrow B} &= -\frac{1}{2}\alpha_B F_A^2 \\ &= -\frac{1}{2}\alpha_B \frac{\mu_A^2}{r^6} (1 + 3 \cos^2 \theta_A). \end{aligned}$$

Similarly, the molecule *B*, which has moment  $\mu_B$ , exerts a field

$$F_B = \frac{\mu_B}{r^3} \sqrt{(1 + 3 \cos^2 \theta_B)},$$

and induces in molecule *A* a moment of magnitude  $\mu_A$ . The energy of interaction between the field due to *B* and the dipole of *A* is

$$\begin{aligned} u_{B \rightarrow A} &= -\frac{1}{2}\alpha_A F_B^2 \\ &= -\frac{1}{2}\alpha_A \frac{\mu_B^2}{r^6} (1 + 3 \cos^2 \theta_B). \end{aligned}$$

The total energy of interaction of the two molecules due to their mutually induced fields and dipoles is

$$\begin{aligned} u &= u_{A \rightarrow B} + u_{B \rightarrow A} \\ &= -\frac{1}{2r^6} \{ \alpha_B \mu_A^2 (1 + 3 \cos^2 \theta_A) + \alpha_A \mu_B^2 (1 + 3 \cos^2 \theta_B) \}. \quad (16) \end{aligned}$$

The net energy of interaction of an ion with the dipole induced by it in surrounding molecules appears to be the chief electrostatic energy involved in the union of oppositely charged ions in the gaseous

phase (p. 114). It has been suggested† that the interaction energy of mutually induced dipoles may be a contributory term in the activation energy of a reaction involving, as so many reactions do, a reactant dipole linked to other dipoles. The transmission, with diminishing magnitude, of electrostatic energy along a chain of linked atoms is certainly capable of interpretation in terms of the induction effect, though it is not always clear whether this energy is capable of being pooled in the activation energy.

† Waters, *loc. cit.*

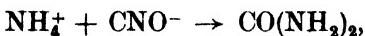
## IV

### REACTIONS BETWEEN IONS

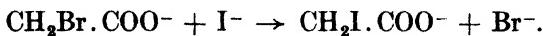
WHEN barium sulphate is formed in solution in the familiar analytical reaction,



the rate of formation is simply the rate at which the barium ions and sulphate ions come together and subsequently fit into the crystal lattice of the precipitated salt. In the crystalline, fused, or dissolved state the sub-molecular constituents of such salts are the ions, which are held together by electrostatic forces. No critical energy is required to render the chemical change complete, and the rate of such true ionic reactions is therefore extremely rapid. In a more general sense, however, we may regard as ionic any chemical change between electrically charged solutes, such, for example, as the transformation of ammonium cyanate into urea,



or the ionic replacement of one halogen atom by another in the substituted acetate ion, e.g.,



It is with reactions of this type that we have now to deal.

#### *The Variation with Temperature of the Dielectric Constant of Liquids*

The application of electrostatic principles to the study of the kinetics of reactions in solution requires, in the first place, a knowledge of the manner in which the dielectric constant of the medium varies with the temperature. Examining a number of somewhat similar liquids, Abegg† concluded that the expression  $D = ce^{-T/190}$  held for them all,  $c$  having a value characteristic of the liquid. Later work, however, has shown that the numerical factor also should be replaced by specific values.‡ In point of fact, the relation

$$D = ce^{-LT}, \quad (1)$$

seems to hold with considerable accuracy for all the liquids examined.

† *Ann. Physik*, **60**, 54, (1897); cf. Abegg and Seitz, *Z. physikal. Chem.*, **29**, 242, (1899); Tangl, *Ann. Physik*, **26**, 59, (1908); Walden, *Z. physikal. Chem.*, **70**, 569, (1908).

‡ Lowry and Jessop, *Trans. Chem. Soc.*, 782, (1930); Åkerlöf, *J. Amer. Chem. Soc.*, **54**, 4125, (1932).

Taking Åkerlöf's data for acetone and the alcohols; those of Morgan and Smyth† for hexane, ethyl bromide, and chlorobenzene; and the remainder from *Tables Annuelles de Constantes données*, (1930 and 1934), we find the values of  $L$  given in Table 1. The constant  $c$  has no relevance for our work. The important factor is  $(LT - 1)$ , according to the sign of which solvents appear to fall into two classes, separated by a third class—not so well defined—for which the term is almost zero at ordinary temperatures.

Table 1

Liquid	$D_{so^{\circ}C}$	$L \times 10^3$	$1/L (^{\circ}\text{abs.})$	$(LT - 1)$ at room temperatures
Toluene	2.347	0.673	1486	Negative
Hexane	1.891	0.714	1401	
Carbon tetrachloride	2.246	0.843	1187	
Benzene	2.282	0.876	1142	
Chlorobenzene	6.649	2.89	346	About zero
Chloroform	4.53	3.33	300	
Acetophenone	18.1	4.1	244	
Anisole	4.35	5.2	192	
Acetone	31.0	4.63	216	Positive
Water	80.0	4.63	216	
Ethyl bromide	9.354	4.91	204	
Nitrobenzene	35.79	5.21	192	
Methyl alcohol	32.47	5.39	188	
Ethyl alcohol	25.0	6.02	166	
Tertiary butyl alcohol	9.705	8.80	114	
Hydrogen chloride	5.13	6.52	153	

### The Evaluation of the Factor $P$ for Ionic Reactions

In the case of bimolecular ionic reactions, the quantity  $A$  of the Arrhenius equation

$$k = Ae^{-E_a/RT} \quad \text{I (4)}$$

differs widely from the normal value of about  $10^{11}$  litres per mole-second. In the first edition of this work it was shown (p. 216) that the ratio of  $A$  to the normal collision frequency could be as high as  $10^{+6}$  or as low as  $10^{-6}$ , but no regularity was then apparent between the signs and charges of the reacting ions and the extent of the departure of the velocities from the standard values. It appeared from later considerations† that abnormal rates may often be due to electrostatic effects. A particularly apposite set of reactions upon

† *J. Amer. Chem. Soc.*, 50, 1547, (1928).

‡ Moelwyn-Hughes and Sherman, *Trans. Chem. Soc.*, 101, (1936).

which to test this hypothesis is afforded by those occurring between ions in solution. We have now to investigate the extent to which an elementary consideration of the electrostatic forces exerted between ions can account for the apparently anomalous rates with which they react in solution.

Normal behaviour coincides with the identity of  $A$  and some standard collision frequency,  $Z$ , which we shall again take to be the value given by the kinetic theory, namely:

$$Z = \frac{N_0}{1000} (r_A + r_B)^2 \left( 8\pi k T \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right)^{\frac{1}{2}}. \quad \text{III (1)}$$

A measure of the departure from normal behaviour is given by the factor  $P$ , defined as

$$P = A/Z. \quad \text{III (4)}$$

Since, by definition,

$$E_A = RT^2 \frac{d \ln k}{dT}, \quad \text{I (11)}$$

the experimental results may be expressed in the form

$$k = P Z e^{-E'/RT}, \quad (2)$$

where

$$E' = E_A - \frac{1}{2}RT. \quad \text{III (2)}$$

Let it now be assumed that the true energy of activation may be resolved into two components,  $E$  and  $E_e$ , the latter denoting the electrostatic contribution to the total energy. Let it further be assumed that chemical change sets in whenever two reacting ions collide with energy equal to or greater than  $(E + E_e)$ . The theoretical velocity for the bimolecular reaction is then†

$$k = Z e^{-(E+E_e)/RT}. \quad (3)$$

Now, if we consider solutions so dilute that the electrostatic interaction energy of two ions is uninfluenced by the presence of other ions,  $E_e$  is readily obtained in terms of their charges and separation. In practice, this ideal condition is realized only at infinite dilution, hence the relevant velocity constants and apparent energies of activation are those found by suitable extrapolation to zero ionic concentration. Such values may be denoted by the superscript zero. In a medium of dielectric constant  $D$ , the energy of interaction of two ions of charges  $z_A \epsilon$  and  $z_B \epsilon$  is  $z_A z_B \epsilon^2 / Dr$ , where  $z$  is the valency

† Christiansen, *Z. physikal. Chem.*, **113**, 35, (1924); Scatchard, *Chem. Rev.*, **10**, 229, (1932).

of the ion, and  $\epsilon$  the electronic charge. Consequently, if  $r$  is the interionic distance at the moment of reaction,

$$E_e^0 = \frac{N_0 z_A z_B \epsilon^2}{Dr}. \quad (4)$$

On comparing these relations with that of the preceding paragraph, we see that

$$E_A^0 = \frac{1}{2}RT + E - \frac{N_0 z_A z_B \epsilon^2}{Dr}(LT - 1) \quad (5)$$

and that

$$P^0 = e^{-E_e^0 L/R} = e^{-z_A z_B \epsilon^2 L/kDr}. \quad (6)$$

In order to test either of these relations† it is necessary to know the value of the critical interionic separation,  $r$ . As this is not always accessible to independent measurement, we may assume equation (6) to be correct, and determine from known values of  $P^0$  the values of  $r$  required to account for them.  $P^0$  values obtained from the literature, after conversion into the appropriate units, are shown in Table 2, the last column of which contains the calculated values of  $r$ . On the whole, these critical distances are reasonable ones, having regard to the frequent impossibility of allowing for the simultaneous effect of temperature, ionic concentration, and concurrent reactions on the velocity. It is to be concluded that the simple electrostatic theory is able to explain in large measure the powerful positive and negative deviations from normal behaviour exhibited by ionic reactions in solution, and that the resolution of the energy into electrostatic and non-electrostatic components is justified *a posteriori*.

### *The Influence of Ionic Strength on the Velocity of Reaction*

Coulomb's expression (equation (4)) for the interaction energy of  $N_0$  isolated pairs of ions holds only when the influence of all other ions in solution is ignored. The calculations of the preceding paragraphs apply therefore to bimolecular velocity coefficients extrapolated at each temperature to infinite dilution or zero ionic strength. When, however, two ions approach each other in an actual electrolytic solution, their interaction energy is, on an average, reduced by an amount  $z_A z_B \epsilon^2 \kappa / D$ , where the reciprocal distance,  $\kappa$ , is related as follows‡ to the ionic strength,  $j$ :

$$\kappa = \epsilon \left( \frac{8\pi N_0 j}{1000 D k T} \right)^{\frac{1}{2}}. \quad (7)$$

† Moelwyn-Hughes, *Proc. Roy. Soc., A*, **155**, 308, (1936).

‡ Debye and Hückel, *Physikal. Z.*, **24**, 185, (1923); **25**, 97, (1924).

Table 2

Reaction	Reference	Ionic type		$P^0$ (observed)	$r$ in Å. (calc.)
		$z_A$	$z_B$		
$[\text{Cr}(\text{H}_2\text{O})_6]^{+++} + \text{CNS}^-$	(1)	+3	-1	$1.09 \times 10^{+8}$	1.56
$[\text{Co}(\text{NH}_3)_6\text{Br}]^{++} + \text{OH}^-$	(2)	+2	-1	$1.39 \times 10^{+6}$	1.38
$\text{NH}_4^+ + \text{CNO}^-$	(3)	+1	-1	$3.83 \times 10^{+1}$	2.63
$\text{XH}^+ + \text{Br}^-$	(4)	+1	-1	$2.46 \times 10^{+1}$	3.00
$\text{XH}^+ + \text{Cl}^-$	(5)	+1	-1	$4.76 \times 10^{+1}$	2.49
$\text{ClO}^- + \text{ClO}^-$	(6)	-1	-1	$3.19 \times 10^{-3}$	1.67
$\text{ClO}^- + \text{ClO}_4^-$	(6)	-1	-1	$2.83 \times 10^{-3}$	1.64
$\text{C}_6\text{H}_5\text{C}(\text{C}): \text{C}(\text{C})\text{COO}^- + \text{I}_3^-$	(7)	-1	-1	$4.83 \times 10^{-4}$	1.31
$\text{CH}_3\text{I}.\text{COO}^- + \text{CN}^-$	(8)	-1	-1	$6.96 \times 10^{-3}$	1.94
$\text{CH}_3\text{I}.\text{COO}^- + \text{CNS}^-$	(8)	-1	-1	$2.19 \times 10^{-3}$	1.57
$\text{CH}_3\text{Cl}.\text{COO}^- + \text{S}_2\text{O}_8^{--}$	(9)	-1	-2	$3.92 \times 10^{-5}$	1.89
$\text{CH}_3\text{Br}.\text{COO}^- + \text{S}_2\text{O}_8^{--}$	(9)	-1	-2	$7.64 \times 10^{-3}$	3.94
$\text{YCl}_4^- + \text{OH}^-$	(10)	-2	-1	$1.95 \times 10^{-5}$	1.68
$\text{YBr}_4^- + \text{OH}^-$	(10)	-2	-1	$1.27 \times 10^{-5}$	1.61
$\text{YI}_4^- + \text{OH}^-$	(10)	-2	-1	$4.30 \times 10^{-6}$	1.48
$[\text{Co}(\text{NH}_3)_6\text{Br}]^{++} + \text{Hg}^{++}$	(2)	+2	+2	$4.30 \times 10^{-4}$	4.96
$\text{AsO}_4^{--} + \text{TeO}_4^{--}$	(11)	-2	-2	$6.77 \times 10^{-6}$	3.23
$\text{S}_2\text{O}_4^{--} + \text{S}_2\text{O}_4^{--}$	(12)	-2	-2	$6.07 \times 10^{-6}$	2.31

(1) Bjerrum, *Z. anorg. Chem.*, **118**, 131, (1921).

(2) Brönsted and Livingston, *J. Amer. Chem. Soc.*, **49**, 435, (1927).

(3) Walker and Hambley, *Trans. Chem. Soc.*, **67**, 746, (1895); Warner and Stitt, *J. Amer. Chem. Soc.*, **55**, 4807, (1933).

(4) Soper and Jones, *Proc. Roy. Soc., A*, **144**, 643, (1934). X stands for chloracetanilide. We consider the velocity of conversion to be too rapid to be explicable on a true ternary collision basis, so we postulate the rate-determining step as above, or  $\text{XCl}^- + \text{H}^+$ , either of which is consistent with the facts.

(5) Harned and Seltz, *J. Amer. Chem. Soc.*, **44**, 1476, (1922).

(6) Foerster, *Z. Elektrochem.*, **23**, 137, (1917); Giardani, *Gazz. chim. Ital.*, **54**, 844, (1924).

(7) Moelwyn-Hughes and Legard, *Trans. Chem. Soc.*, **424**, (1933).

(8) Wagner, *Z. physikal. Chem., A*, **115**, 121, (1925).

(9) Kappanna, *J. Indian Chem. Soc.*, **9**, 382, (1932).

(10) Panepinto and Kilpatrick, *J. Amer. Chem. Soc.*, **59**, 1871, (1937). The complex ions are the tetra-halogeno-phenolsulphonephthaleins, or halogenophenol blues.

(11) Straup and Meloche, *ibid.*, **53**, 3331, (1931).

(12) Jellinek and Jellinek, *Z. physikal. Chem.*, **93**, 325, (1919).

$N_0$  and  $k$  are the constants of Avogadro and Boltzmann.  $\epsilon$  is the electronic charge. The ionic strength is defined† in terms of the valencies,  $z_i$ , and the molalities,  $c_i$  (in gram-ions per kilogram of solvent), of all the ionic species present, according to the relation

$$j = \frac{1}{2} \sum c_i z_i^2. \quad (8)$$

The average energy of interaction of a pair of ions separated by a

† Lewis and Randall, *J. Amer. Chem. Soc.*, **43**, 1112, (1921).

distance  $r$  in solution is thus a function of the concentration and the solvent, and is

$$\frac{E_e}{N_0} = \frac{z_A z_B \epsilon^2}{Dr} (1 - \kappa r), \quad (9)$$

which reduces to the simple Coulombic expression only when  $\kappa = 0$ , that is, at infinite dilution. The theory of Debye and Hückel rests on a number of assumptions, including the assumption of complete dissociation, and in the present approximate form is known from extra-kinetic sources to be restricted in validity to very dilute solutions. Into a discussion of the various elaborations of the theory† we do not propose to enter. We have merely to discover how far the present theory can predict the effect of ionic strength on the velocity of reaction between charged particles in solution.

Let it be assumed, as before, that chemical change sets in when the reacting ions collide with energy equal to or greater than  $E + E_e$ , where for  $E_e$  we now adopt equation (9) given by the simple theory. The expression for the bimolecular velocity coefficient is then

$$k = Ze^{-E/RT} e^{-(z_A z_B \epsilon^2 / Dr kT)(1 - \kappa r)}. \quad (10)$$

If interest is confined to a given reaction, and to the effect of ionic concentration on its rate at a given temperature, then clearly

$$k = k^0 e^{+z_A z_B \epsilon^2 \kappa / DkT}, \quad (11)$$

where  $k^0$  is the velocity coefficient for that reaction at that temperature, and corresponding to zero ionic concentration. It is the specific coefficient discussed in the preceding section. Taking logarithms, we have

$$\log_{10}(k/k^0) = qz_A z_B \sqrt{j}, \quad (12)$$

where, according to equation (7),

$$q = \frac{\epsilon^2}{2 \cdot 303 DkT} \left\{ \frac{8\pi N_0}{1000 DkT} \right\}^{\frac{1}{2}}. \quad (13)$$

The application of the interionic attraction theory of electrolytes to the problem of the velocity of ionic reactions at a given temperature thus leads to the conclusions that (1) the logarithm of the velocity coefficient is a linear function of the square root of the ionic strength, (2) the gradient of the  $\ln k - \sqrt{j}$  curve is positive for reactions occurring between ions charged with the same sign ( $z_A z_B$  is positive) and negative for reactions between oppositely charged particles ( $z_A z_B$  is negative), (3) in a given solvent at a given temperature, the gradients,

† e.g. Gronwall, *Proc. Nat. Acad. Sci.*, **13**, 198, (1927).

$d \log_{10} k/d(\sqrt{j})$ , for all ionic reactions are an integral multiple of a constant quantity,  $q$ , which is given explicitly by the theory.

These interesting generalizations on the influence of ionic environment at a constant temperature were derived by Brönsted† from a thermodynamic treatment of the equilibrium postulated between the reacting ions and a charged reactive complex, for the activity coefficient of each of which the theoretical expression of the interionic attraction theory was employed. Their verification also is due chiefly to him and his collaborators. The statistical treatment given here follows that of Christiansen.‡

In order to test these relations we require information concerning the velocity of reactions of various ionic types (i.e. various values of  $z_A z_B$ ) in different solvents over ranges of temperature. Most of the experimental material, until quite recently, has been confined to work in aqueous solutions at the temperature 298.1°, under which conditions it happens that the term  $q$  of equation (13) is 1.01. In water at this temperature, therefore, the approximate requirement of the theory is that

$$\log_{10}(k/k^0) \doteq z_A z_B \sqrt{j}. \quad (14)$$

The first five reactions to be considered in the light of this relation are the saponification of the nitrourethane ion,§ the oxidation of hydrobromic acid by hydrogen peroxide,|| the reaction of brompentammine cobaltic ion with the mercuric and hydroxyl ions,†† and the reaction between the thiosulphate and bromacetate ions.†† The results of the various investigations are shown graphically in Fig. 1, which is taken from an admirable summary by Livingston. §§ The results obtained by King and Jacobs||| for the reaction between the iodide and persulphate ions are also shown, as superimposed by them upon the earlier graph. The straight lines are the nearly integral slopes required by equation (14).

Reactions between ions and polar molecules are discussed in the next chapter, but, for the sake of completeness, one set of data is

† *Z. physikal. Chem.*, **102**, 109, (1922); **115**, 337, (1925); *Chem. Rev.*, **5**, 231, (1928).

‡ *Z. physikal. Chem.*, **113**, 35, (1925). The term  $N_0$  has been accidentally omitted from equation (17) of this paper. See also Scatchard, *Chem. Rev.*, **10**, 229, (1932).

§ Brönsted and Delbonco, *Z. anorg. Chem.*, **144**, 248, (1925).

|| Livingston, *J. Amer. Chem. Soc.*, **48**, 53, (1926).

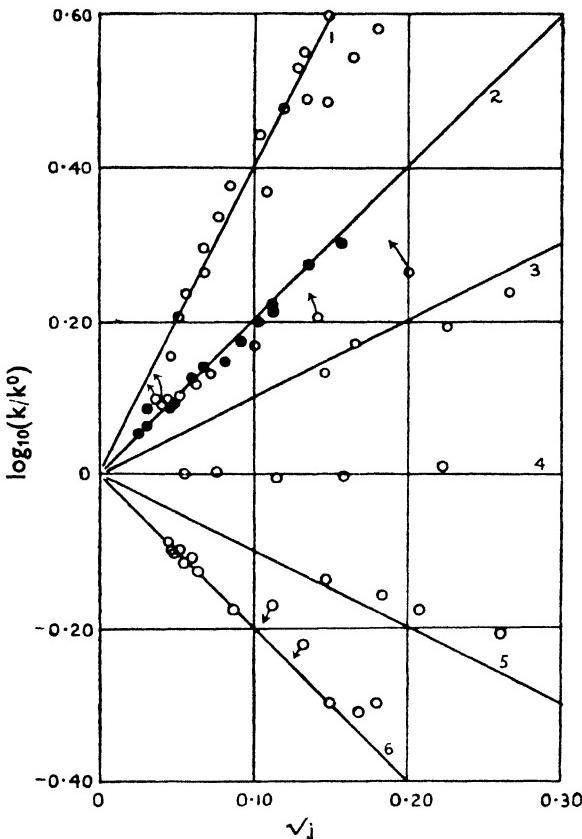
†† Brönsted and Livingston, *ibid.*, **49**, 435, (1927).

†† Kappanna, *J. Indian Chem. Soc.*, **6**, 45, (1929); La Mer, *J. Amer. Chem. Soc.*, **51**, 3341, 3678, (1929).

§§ *J. Chem. Education (Canada)*, **7**, 2887, (1930).

||| *J. Amer. Chem. Soc.*, **53**, 1704, (1931).

included here. It refers to the saponification of ethyl acetate in aqueous solution at 297.8°. From the following figures,† the electro-



1.  $2[\text{Co}(\text{NH}_3)_5\text{Br}]^{++} + \text{Hg}^{++} + 2\text{H}_2\text{O} \rightarrow 2[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{+++} + \text{HgBr}_2$ .
2. Circles.  $\text{CH}_3\text{BrCOO}^- + \text{S}_2\text{O}_8^{2-} \rightarrow (\text{CH}_3\text{S}_2\text{O}_8\text{COO})^{--} + \text{Br}^-$ .  
Dots.  $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$ .
3.  $[\text{NO}_2 = \text{N} - \text{COOC}_2\text{H}_5]^- + \text{OH}^- \rightarrow \text{N}_2\text{O} + \text{CO}_3^{2-} + \text{C}_2\text{H}_5\text{OH}$ .
4.  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{C}_2\text{H}_5\text{OH}$ .
5.  $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Br}^- \rightarrow 2\text{H}_2\text{O} + \text{Br}_2$ .
6.  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{++} + \text{OH}^- \rightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{+++} + \text{Br}^-$ .

FIG. 1. The influence of ionic strength on the velocity of ionic reactions.

lyte effect is seen to be almost absent within the explored concentration region:

$[\text{NaOH}] \times 10^3$ , moles/litre	3.16	6.25	12.5	25.0	50.0
$k \times 10$ , litres/mole.sec.	1.10	1.10	1.07	1.08	1.14

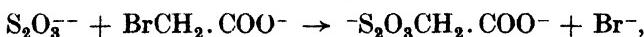
† Arrhenius, *Z. physikal. Chem.*, 1, 111, (1887).

The behaviour is consistent with the theoretical anticipation for reactions between ions and uncharged molecules ( $z_A z_B = 0$  in equation (11)).

It is clear from an examination of Livingston's graph that in no case are the experimental results far removed from the predictions of the theory. We may with profit, however, consider one or two cases in greater detail.

According to equation (14), the slope of the curve found by plotting  $\log_{10} k$  against  $\sqrt{j}$  for a reaction between oppositely charged univalent ions in water at  $298\cdot 1^\circ$  should be  $-1$ . In view of the experimental difficulties, the gradient found in the case of the reaction between hydrobromic acid and hydrogen peroxide (curve 5, Fig. 1) must be regarded as in satisfactory agreement with the requirements of this equation. A reaction of the same ionic type which is probably less complicated is the conversion of ammonium cyanate into urea. Walker and Hambly (*loc. cit.*) concluded from a study of the effect of adding electrolytes that the reaction took place between the ammonium and cyanate ions, but other views concerning the mechanism have been held.<sup>†</sup> As this reaction was the first ionic reaction in solution to which the collision theory appeared to apply,<sup>‡</sup> let us consider the original data in the light of Brönsted's theory. With a decinormal solution of the salt at  $353\cdot 2^\circ$ , the investigators found a bimolecular velocity coefficient of  $2\cdot 40 \times 10^{-3}$  litres/mole-second; at double the dilution,  $k$  became  $2\cdot 73 \times 10^{-3}$ . In this concentration region, therefore, the gradient is  $-0\cdot 61$ . The value calculated from equations (12) and (13) is  $-0\cdot 67$ . The supposition that the measurable reaction is that between the ions is thus confirmed. Within recent years the reaction has again been carefully investigated in media of different dielectric constants, at different temperatures and ionic strengths, with confirmatory results.<sup>§</sup>

According to equation (14), the plot of  $\log_{10} k$  against  $\sqrt{j}$  should be linear, with a gradient of  $+2$  for all bimolecular reactions between univalent anions and bivalent anions in water at  $298\cdot 1^\circ$ . The reaction



which is kinetically bimolecular,<sup>||</sup> is subject to a pronounced positive

<sup>†</sup> e.g. by Chattaway, *Trans. Chem. Soc.*, **67**, 746, (1895).

<sup>‡</sup> Moelwyn-Hughes, *Chem. Rev.*, **10**, 241, (1932).

<sup>§</sup> Warner and Stitt, *loc. cit.*; Warner and Warrick, *J. Amer. Chem. Soc.*, **57**, 1491, (1935); Svirbely and Warner, *ibid.*, **57**, 1883, (1935).

<sup>||</sup> Slator, *Trans. Chem. Soc.*, **87**, 485, (1905).

electrolyte effect, as is seen from the data† of Table 3, but the curve found by plotting  $\log_{10} k$  against  $\sqrt{j}$  is not linear. We must therefore conclude either that the theory is not applicable within this range of ionic concentration or that the reaction is attended by complications. The gradient of the curve in the intermediate region is about +0.7, but if we consider only the two points corresponding to the lowest concentrations, we obtain analytically the experimental gradient of

Table 3

*The Influence of Concentration on the Velocity of the Thiosulphate-Bromacetate Reaction*

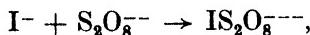
[S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ] (moles/litre)	[BrCH <sub>2</sub> .COO <sup>-</sup> ] (moles/litre)	j	k × 10 <sup>3</sup> (litres/mole-second)
0.01	0.01	0.04	7.6
0.01	0.02	0.05	8.4
0.02	0.01	0.08	8.4
0.05	0.05	0.20	11.6
0.25	0.25	1.00	17.6

+1.84, which is only 8 per cent. lower than that anticipated on theoretical grounds. More recent work on the electrolyte effect in diluter solutions‡ appeared at first to give the theoretical slope exactly, but on properly computing the ionic strengths§ it appeared that the maximum experimental slope is only +1.5. Kappanna and Patwardhan,|| however, realized the theoretical slope at values of j below 0.012, and further vindication of the limiting law has been obtained by Fräulein von Kiss and Vass.††

The second reaction of this type which we shall discuss is that between the iodide and persulphate ions, the net chemical change being that represented by the equation



The order of reaction as determined by the method of initial rates (equation II(17)) is 2.4, and by the method of isolation is 2.0.‡‡ A possible mechanism is that the measurable reaction is the formation of a triply charged anion



† Krapiwin, *Z. physikal. Chem.*, **83**, 439, (1913).

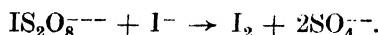
‡ La Mer, *J. Amer. Chem. Soc.* **55**, 1739, (1933).

§ *Idem, ibid.*, p. 3678. || *J. Indian Chem. Soc.*, **9**, 379, (1932).

†† *Z. anorg. Chem.*, **217**, 305, (1934).

‡‡ Price, *Z. physikal. Chem.*, **27**, 474, (1898).

followed by the rapid change



Various methods have been employed to measure the rate of reaction. Price titrated the iodine produced against standard sodium thiosulphate. King and Jacobs† first decolorized the reacting solution with thiosulphate, and, by means of a photoelectric colour detector, measured the time required by the liberated iodine to colorize the solution. As shown in Fig. 1, their results conform with Brönsted's theory. An equally careful reinvestigation,‡ using the original titration method, yielded the following results (Table 4) for the bimolecular velocity coefficient extrapolated to zero time. The results are plotted in Fig. 2, which shows a linear slope of +2.42.

*Table 4*  
*The Influence of Concentration on the Velocity of the*  
*Persulphate-Iodide Reaction*

[I <sup>-</sup> ] (moles/litre)	[S <sub>2</sub> O <sub>8</sub> <sup>--</sup> ] (moles/litre)	$\sqrt{j}$	$k \times 10^3$ (litres/mole-second)
0.00040	0.00020	0.03162	1.04
0.00900	0.00045	0.04743	1.08
0.00339	0.00020	0.06324	1.18
0.00160	0.00180	0.06324	1.21
0.00250	0.00125	0.07905	1.29
0.00840	0.00020	0.09486	1.35
0.00360	0.00180	0.09486	1.39
0.00490	0.00245	0.11067	1.54
0.01541	0.00020	0.12648	1.72
0.00640	0.00320	0.12648	1.69
0.00910	0.00405	0.14229	1.97
0.02440	0.00020	0.15810	2.03
0.01000	0.00500	0.15810	2.05

A determination of the gradients by the method of least squares for the three sets of experimental points shows that this figure is reproducible to within  $\pm 0.06$ . The difference between the two observations may, as Soper and Williams point out, be due to the photolytic decomposition of the persulphate ion in King and Jacobs's experiments, and partly to the complicating effect of added thiosulphate and starch. On the other hand, the titration method is not entirely free from objections, though it probably gives the more reliable result. It must not be overlooked that according to the mechanism

† *J. Amer. Chem. Soc.*, **53**, 1704, (1931).

‡ Soper and E. Williams, *Proc. Roy. Soc., A*, **140**, 59, (1933).

outlined above, the complex ion may attain a stationary concentration (p. 16) determined by the relation

$$+\frac{d[X]}{dt} = k_2[I^-][S_2O_8^{2-}] - k_1[X] - k_3[I^-][X^-] = 0,$$

whence the rate of production of iodine molecules becomes

$$+\frac{d[I_2]}{dt} = k_3[I^-][X^-] = \frac{k_2[I^-][S_2O_8^{2-}]}{1 + (k_1/k_3)[I^-]}.$$

This relation is consistent with a reaction of variable kinetic order, changing from the second order at high concentrations of iodide ion

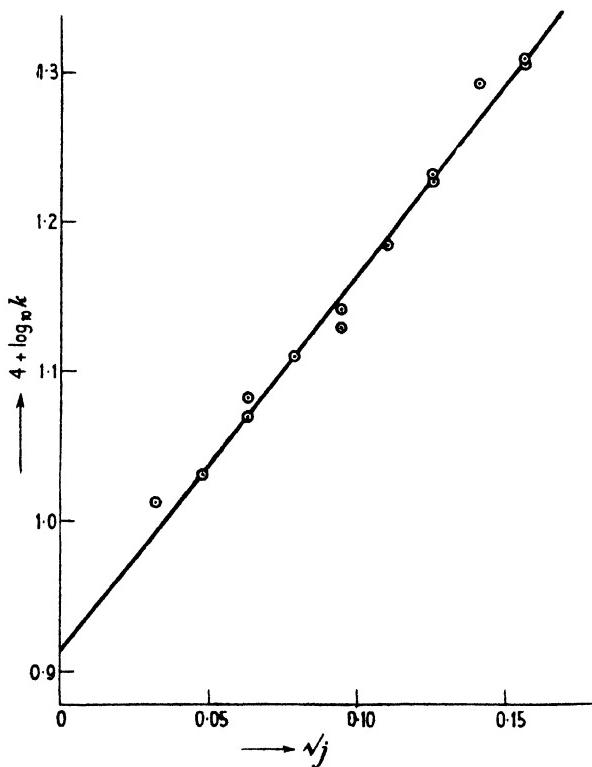


FIG. 2. Influence of ionic strength on the velocity of the persulphate-iodide reaction.

to the third order at low concentrations. Particular interest, therefore, attaches to the conclusion of Howells† that this reaction is anomalous in the sense that the factor  $P$  cannot be explained as it

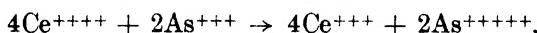
† *Trans. Chem. Soc.*, 641, (1941).

can in all other cases of ionic reactions. Since  $k_{298.1}^0$  is  $8.29 \times 10^{-4}$  litres/gram molecule-second, we would anticipate an  $E_A$  value of about 17,000 calories; this greatly exceeds that found by Howells, which varies from 12,330 to 12,520, according to the nature of the cation.

For the reaction between the hydroxyl and brompentammine-cobaltic ions (curve 6, Fig. 1), Brönsted and Livingston† find that at  $j = 0.033$ , the slope is already 0.84 times the value of -2 required by the Debye-Hückel expression.

It is to be concluded that in general equation (12) always accounts correctly for the qualitative effect of the electrolyte concentration on the velocity of ionic reactions, and is able to account quantitatively, to within some 20 per cent., for the electrolyte effect. The position of the Brönsted theory may, in fact, be now regarded as so firmly established that it could be used with some confidence to elucidate the mechanism of ionic reactions wherein only one of the valencies is known.

It would be a matter of great interest to obtain results for bimolecular reactions of still higher ionic type, but few experimental attempts in this direction have been made. The rate of reduction of the ferric ion by stannous ion,‡ for which  $z_A z_B = 6$ , is not governed by the frequency of collisions between them. A preliminary study of the oxidation of the ferrocyanide ion by the persulphate ion§ reveals many of the features of a typical ionic reaction, though the results are not sufficiently free from ambiguity to test the theory for the high ionic types ( $z_A z_B = 8$ ). Thus in the lowest concentration region explored ( $c_A = c_B = 0.00625 - 0.025$ , or  $\sqrt{j} = 0.285 - 0.570$ ), which is beyond the realm of applicability of equation (12), the gradient is linear, in the anticipated direction, but is only 2.7. Reactions with still higher values of  $z_A z_B$  are



and the similar oxidation of ferrous by ceric salts, which proceed in hot aqueous solution.||

### *The Relation between the Apparent Energy of Activation and the Ionic Strength*

It is a simple matter to obtain the formal relations for the dependence of both  $E_A$  and  $P$  on the ionic strength in solutions where the

† *Loc. cit.*

‡ Gorin, *J. Amer. Chem. Soc.*, **58**, 1787, (1936).

§ Holluta and Herrmann, *Z. physikal. Chem.*, A, **166**, 453, (1933).

|| I am indebted to my colleague, Mr. A. J. Berry, for these suggestions.

expression of Debye and Hückel holds for the free energy of the reacting ions. Substituting into equation (10) the expressions for  $Z$ ,  $D$ , and  $\kappa$  given by equations III(1), IV(1), and IV(7), and comparing with the semi-empirical equation I(4), we obtain the following relations:

$$E_A = \frac{1}{2}RT + E - \frac{N_0 z_A z_B \epsilon^2}{Dr} (LT - 1)(1 - \frac{3}{2}\kappa r) \quad (15)$$

and  $P = e^{-z_A z_B \epsilon^2 L/kDr} e^{(z_A z_B \epsilon^2 \kappa/2DkT)(3LT-1)}$ , (16)

which may conveniently be written as follows:

$$E_A = E_A^0 + \frac{3 N_0 z_A z_B \epsilon^2 \kappa}{D} (LT - 1) \quad (17)$$

and  $P = P^0 e^{(z_A z_B \epsilon^2 \kappa/2DkT)(3LT-1)}$ , (18)

in which  $E_A^0$  and  $P^0$  have the values given by equations (5) and (6) respectively. Although both these relations appear to be independent of the variable  $r$ , the critical separation, only the former is in fact so, because some reasonable value of  $r$  is assumed in the present evaluation of the factor  $P$ . We shall therefore consider equation (17) chiefly. In the region to which the theory applies, the Arrhenius constant is seen to be a linear function of the square root of the ionic strength.  $E_A$  should be unaffected by the electrolytic concentration for reactions between ions and uncharged molecules. Instances conforming to this rule will be cited in the next chapter. Many possibilities exist for the reactions of charged particles in different solvents, for not only can  $z_A z_B$  have positive and negative values for the various reactions but the term  $(LT - 1)$  also may have positive and negative values in the different solvents. Most existing data refer, however, to the ordinary ionizing solvents, for which, as we have seen, the term  $(LT - 1)$  is positive.

Let us first consider the order of magnitude of the change in the apparent energy of activation which is to be expected in aqueous solution at  $298.1^\circ$ . Recalling the definition of  $\kappa$ , equation (17) in its complete form is

$$E_A = E_A^0 + \frac{3 N_0 z_A z_B \epsilon^3 (LT - 1)}{D} \left\{ \frac{8\pi N_0}{1000 D k T} \right\}^{\frac{1}{2}} \sqrt{j}. \quad (19)$$

With  $D = 78.8$ ,  $L = 4.63 \times 10^{-3}$ , and with the energy expressed in calories, we have

$$E_A = E_A^0 + 800 z_A z_B \sqrt{j}. \quad (20)$$

Equation (9) is probably valid for values of  $\sqrt{j}$  lying below 0.01, hence

the order of magnitude of the change in  $E_A$  which may be expected is 100 calories. It is only since these relations were first derived† that data of sufficient precision have become available to test them. As shown by some typical instances in Table 5, equation (19) seems to account correctly for the sign and magnitude of the observed changes.

*Table 5*  
*The Dependence of  $E_A$  on Ionic Strength in Aqueous Solution*

Reaction	$z_A z_B$	$T$	$j_1$	$j_2$	$(E_A)_1$	$(E_A)_2$	$(E_A)_2 - (E_A)_1$	Observed	By equation (19)
$\text{NH}_4^+ + \text{CNO}^-$	-1	323.1	—	0.3760	23,580	23,240	-340†	-265	
$\text{S}_2\text{O}_3^{2-} + \text{BrCH}_2\text{COO}^-$	+2	285.6	0.0080	0.0200	15,881	16,009	+128‡	+123	
$\text{Br}_4\text{Y}^{4-} + \text{OH}^-$	+2	288.1	—	0.0023	12,400	12,439	+39§	+58	
			(0.0023)	0.0086	12,439	12,470	+31§	+54	

† Svirbely and Warner, *J. Amer. Chem. Soc.*, **57**, 1883, (1935).

‡ La Mer and Karmer, *ibid.*, p. 1674.

§ La Mer and Amis, *J. Franklin Inst.*, **225**, 709, (1938); Panepinto and Kilpatrick, *loc. cit.*

Since, however, the experimental error even in precise determinations of  $E_A$  is about  $\pm 30$  calories, further data on reactions of higher ionic type are needed to consolidate the position.

#### *The Variation of the Apparent Energy of Activation with Temperature*

We have seen in Chapter II that the many reactions for which the term  $E_A$  of the Arrhenius equation is constant over fairly wide temperature ranges include the synthesis of urea. We have now to discover whether the mechanism of ionic reactions assumed here leads to a temperature-invariant value of  $E_A$ , or whether the constancy observed in this particular instance is apparent only, due to the limits of experimental certainty.

Upon differentiating equation (15) with respect to temperature, while keeping the ionic strength constant, we obtain the following relation:

$$\left(\frac{dE_A}{dT}\right)_j = \frac{1}{2}R - \frac{N_0 z_A z_R \epsilon^2}{Dr} \{L^2 T - \frac{3}{2}kr(LT-1)^2\}. \quad (21)$$

The temperature dependence of the apparent energy of activation has been very thoroughly examined in the case of the reaction between the thiosulphate and bromacetate ions. From the data of Kappanna‡ an approximate value of -25 calories/mole-degree is found, but as later workers have noted, this effect, although fairly consistent, is

† *The Kinetics of Reactions in Solution*, 1st ed., p. 199, (1933).

‡ *J. Indian Chem. Soc.*, **6**, 45, (1929).

rather less than the experimental error of his work. A more reliable figure is that of  $-13$  obtained from the work of Fräulein von Kiss and Vass.<sup>†</sup> Still greater refinements can be claimed by La Mer and Kammerer,<sup>‡</sup> from whose data the apparent energies of activation for this reaction at different temperatures and ionic strengths have been abstracted (Table 6). The values at the lower concentration are for solutions containing  $0\cdot005$  moles per litre of the two reactants, and at the higher concentration for solutions containing the same number of moles of reactants with  $0\cdot06$  moles of barium chloride per litre. In agreement with the requirement of equation (21), the apparent energy of activation under these conditions decreases as the temperature is raised. In aqueous solution at  $291\cdot85^\circ$  for reactions with  $z_A z_B = +2$ , equation (21) becomes

$$\left(\frac{dE_A}{dT}\right)_j = 0\cdot99 - \frac{51\cdot6}{r(\text{\AA})} + 1\cdot72\sqrt{j}, \quad (22)$$

where  $E_A$  is again expressed in calories per gram mole, and  $r$  is now given in Ångstrom units. In regions where the Debye-Hückel law holds the anticipated change in  $E_A$  is thus small. Taking an average

Table 6

*The Variation of the Apparent Energy of Activation with Temperature in the Case of the Thiosulphate-Bromacetate Reaction*

$T$	$j = 0\cdot02$ ( $1/\kappa = 21\cdot5 \text{ \AA.}$ )		$j = 0\cdot20$ ( $1/\kappa = 6\cdot8 \text{ \AA.}$ )	
	$E_A$	$(dE_A/dT)_j$	$E_A$	$(dE_A/dT)_j$
279·35	16,072	-10·1	16,353	-17·4
291·85	15,946	-7·2	16,136	-21·8
304·35	15,856		15,864	

value of  $dE_A/dT = -8\cdot7$  at the lower concentration, the critical separation becomes  $2\cdot41 \text{ \AA.}$  Taking the average value of

$$dE_A/dT = -19\cdot6$$

at the higher concentration,  $r$  becomes  $5\cdot19 \text{ \AA.}$  It is doubtful, however, whether the theory or the experiments can stand the strain of such a detailed analysis. Even assuming an absolute accuracy in the temperature,  $dE_A/dT$  may well be in error by about  $\pm 5$  calories/mole-degree. The mean of all values given in Table 6 is  $-15\cdot6$ , from which,

<sup>†</sup> *Z. anorg. Chem.*, **217**, 305, (1934).

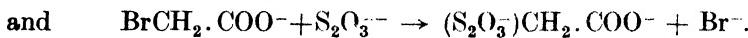
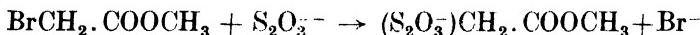
<sup>‡</sup> *J. Amer. Chem. Soc.*, **57**, 2662, (1935).

according to equation (22), the critical separation becomes 3.31 Å. This figure is not only a reasonable one in itself, but compares favourably with that independently obtained in Table 2.

We may here conveniently describe still another method which has been employed† to evaluate the critical ionic separation from kinetic data. From the definition of the term  $k^0$  implicit in equations (10) and (11), we obtain the relation

$$\ln k^0 = \ln Z - \frac{E}{RT} - \frac{z_A z_B \epsilon^2}{DrkT}. \quad (23)$$

As stated in an earlier section of this chapter, most ionic reactions are chemical changes occurring between charged particles, and the same metathesis can and often does occur when one of the particles is uncharged. The thiosulphate ion, for example, replaces a halogen attached to a saturated carbon atom more readily from an uncharged molecule, such as an ester, than from a similarly charged ion, such as a fatty acid anion. Consider the two reactions



If we may assume the terms  $E$  and  $Z$  to have common values for both reactions, then

$$\log_{10}\left(\frac{k_{\text{ester}}^0}{k_{\text{ion}}^0}\right) = \frac{z_A z_n \epsilon^2}{2.303 DrkT}. \quad (24)$$

Substituting numerical values for the constants relating to water at 298.1°, the expression becomes  $z_A z_B \times 3.066 \times 10^{-8}/r$ . The limiting value of the ratio of the velocity coefficients determined experimentally by La Mer is 58, whence  $r = 3.47$  Å.

### *The Critical Ionic Separation*

We have in this chapter studiously avoided any reference to ionic diameters, preferring to make use of the distance,  $r$ , to which a pair of ions must approach each other before they can undergo chemical change. Three experimental methods which have emerged from the electrostatic theory of reaction velocity for the experimental determination of this critical separation have been applied to the thiosulphate-bromacetate reaction in water, and a fourth method—to be described below—has been applied to another ionic reaction. As far as the results obtained in the former case are concerned (Table 7),

† La Mer, *Chem. Rev.*, **10**, 179, (1932).

it is seen that the various values of  $r$  are reasonable in themselves and agree fairly well with one another. We are thus very far removed

Table 7

*The Critical Ionic Separation in the Reaction between the Thiosulphate and Bromacetate Ions in Aqueous Solution*

Method	Equation	$r \times 10^8$ (cm.)
The absolute magnitude of $P$ at zero ionic strength	6	3.94
The variation of $E_A$ with respect to temperature at constant ionic strength	21	3.31
The comparison of the rates of the ion-ion and the ion-molecule reactions	24	3.47

from the early applications of the collision theory to the problem of reaction kinetics in solution, when the first step in any theoretical approach was an attempt to find, from extra-kinetic sources, a reasonable value for the molecular or ionic 'radius'. The acceptance of the experimental value of  $r = 3.6 \text{ \AA}$ . for the critical ionic separation, and of the cited value for the critical increment of energy is, in the example studied, sufficient completely to account for all the peculiarities of the reaction velocity under the varying conditions of temperature, ionic environment, and dielectric constant.

#### *Ionic Reactions in Non-Aqueous Solvents*

Relatively little information is available on the kinetics of ionic reactions in non-aqueous solvents. Before examining the results obtained for the reaction between the cyanate and monomethylammonium ions in ethylalcoholic solution, let us consider the effect upon the velocity coefficient of an ionic reaction in aqueous solution when the water is gradually replaced by methyl alcohol, ethyl alcohol, glucose, or any other apparently inert medium of different dielectric constant. If the velocity coefficient appertaining to zero ionic strength can be found for a given reaction in a series of media with different dielectric constants, we obtain, † by differentiation of equation (10),

$$\frac{\partial \log_{10} k^0}{\partial (1/D)} = - \frac{z_A z_B \epsilon^2}{2.303 r k T}, \quad (25)$$

provided both  $E$  and  $Z$  are independent of the medium. La Mer and Amis‡ have studied the hydrolysis of the divalent anion of bromphenol blue in the light of this relation. At  $298.1^\circ$ , the desired

† Scatchard, *ibid.*, p. 229, (1932).

‡ *Loc. cit.*

linear relation has been found experimentally, while  $D$  is varied from 78 to about 68 by the addition of alcohol. The sign and magnitude of the gradient are in agreement with equation (25), which, under these conditions, becomes  $d \log_{10} k / d(1/D) = -4.84 \times 10^{-6}/r$ . The experimental slope appears to be  $-3.2 \times 10^{-2}$ , whence  $r$  becomes 1.50 Å., in satisfactory agreement with the results of Panepinto and Kilpatrick, cited in Table 2 (La Mer and Amis give  $r = 2.6$  Å., but their graph, from which these figures are taken, appears to give the lower value). The assumption that  $E$  and  $Z$  do not vary while the medium is changed to this extent seems therefore to be justified. Similar investigations have been carried out on the reaction between the cyanate and ammonium ions.†

The differentiation of equation (10) which led to equation (15) was carried out at constant pressure and ionic strength. When differentiating equation (10) with respect to  $T$ , while keeping  $P$ ,  $\kappa$ , and also  $D$  constant, we obtain

$$E_D = RT^2 \left( \frac{d \ln k}{dT} \right)_{P, \kappa, L} = \frac{1}{2}RT + E + \frac{N_0 z_A z_B \epsilon^2}{Dr} (1 - \frac{3}{2}\kappa r), \quad (26)$$

which is naturally the expression to which (15) reduces when  $L$  is zero. Values of  $D$  may be kept constant by changing the composition of the solvent. By subtraction, we have

$$E_D - E_A = \frac{N_0 z_A z_B \epsilon^2 LT}{Dr} (1 - \frac{3}{2}\kappa r), \quad (26a)$$

which has been verified experimentally for a variety of reactions by Amis‡ and his collaborators.§

The reaction



has been investigated kinetically in aqueous|| and in ethylalcoholic solution.†† In aqueous solution at 312.98°,  $\log_{10} k$  plotted against  $\sqrt{j}$  gives a gradient of about  $-0.63$  at  $\sqrt{j} = 0.20$  and of  $-0.77$  at  $\sqrt{j} = 0.17$ . Thus the experimental slope approaches, but is somewhat lower than, the theoretical value of equation (12). There can be no doubt, however, that, as in the case of the unsubstituted reaction,

† Warner and collaborators, *loc. cit.*

‡ *J. Amer. Chem. Soc.*, **63**, 1606 (1941).

§ Amis and S. E. Cook, *ibid.*, p. 2621; Amis and F. C. Holmes, *ibid.*, p. 2231; Amis and J. E. Potts, *ibid.*, p. 2883.

|| Miss C. C. Miller, *Proc. Roy. Soc., A*, **145**, 288, (1934).

†† *Idem, ibid.*, **151**, 189, (1935).

the rate of chemical change is governed by the frequency of collisions between the oppositely charged ions. Taking the ionic mobilities of the cyanate and monomethylammonium ions at  $313.1^\circ$  as 78 and 83 respectively, the radii become  $1.50 \text{ \AA}$ . and  $1.60 \text{ \AA}$ ., hence  $r = 3.10 \text{ \AA}$ . With this value,  $E$  becomes 21,990, and equations (10) and III(1)

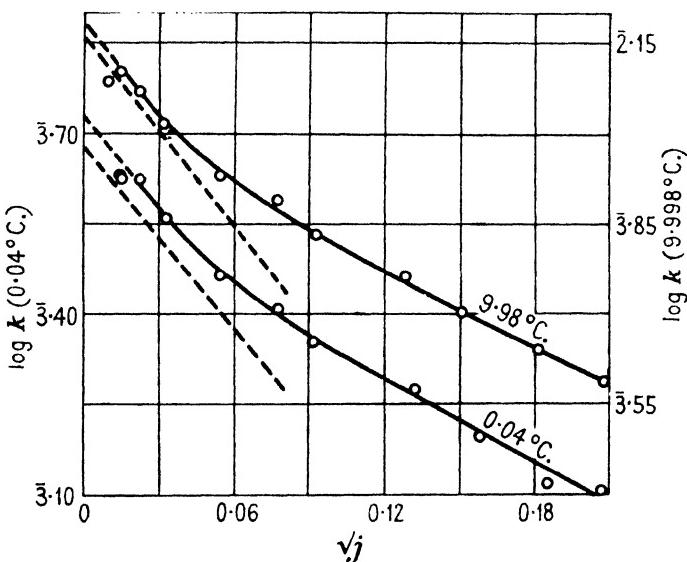


FIG. 3.

account satisfactorily for the velocity coefficients. At the same temperature in ethylalcoholic solution, the reaction velocity is about 540 times as fast. The dependence of  $\log_{10} k$  upon  $\sqrt{j}$  is shown in Fig. 3, which is taken from Miller's paper. The dotted lines represent the theoretical slopes given by equation (12). The experimental points congregate round the theoretical slope at concentrations below one millimole of salt per litre. Omitting some points at great dilutions, Miller estimates  $k^0 = 6.73 \times 10^{10} \times e^{-16370/RT}$  litres/mole-second. As the extrapolation is somewhat arbitrary, we have interpolated in Table 8 some velocity coefficients at the two temperatures and at rounded concentrations. In the explored concentration region,  $E_A$  on the whole increases as  $j$  is raised. This is contrary to what one would expect if equation (12), and consequently equation (19), apply. But we have seen that the theoretical law is approximated to only at concentrations below  $10^{-3}$ , and a possible variation of  $E_A$  in the correct direction is not excluded in this region, as the figures of

Table 8

*The Influence of Ionic Strength on the Velocity Coefficient and Apparent Energy of Activation of the Reaction between  $\text{CH}_3\text{NH}_3^+$  and  $\text{CNO}^-$  in  $\text{C}_2\text{H}_5\text{OH}$*

$c \times 10^3$ (moles/litre)	$k \times 10^3$ (litres/mole-second)		$E_A$
	At 283.08°	At 273.14°	
0	(13.4)	(4.44)	(17,060)
1	10.6	3.60	16,680
2	9.40	3.18	16,740
4	8.20	2.76	16,810
7	7.20	2.39	17,070
10	6.46	2.16	16,920
15	5.73	1.91	16,970
20	5.24	1.71	17,300
30	4.49	1.41	17,890
40	4.00	1.26	17,840

Table 8 shows. Too much reliance, however, must not be placed in one direction or another on results which are limited to a temperature region of only 10 degrees. With the present extrapolated value of  $E_A$ , we have  $k^0 = 1.98 \times 10^{11} \times e^{-E_A/RT}$ . Making allowance for the restricted range of conditions and for the experimental difficulties, the results of the investigation fully support the application of the simple theory of ionic reactions to non-aqueous solvents. Much work, however, in this direction awaits completion before the position can be regarded as satisfactory.

#### *Apparent Exceptions to the Brönsted Relation*

We have seen that the observed variation with ionic strength of reactions belonging to all the investigated ionic types can be represented to within some  $\pm 20$  per cent. by Brönsted's relation (12). Certain exceptions, reported in the literature, may now be discussed.

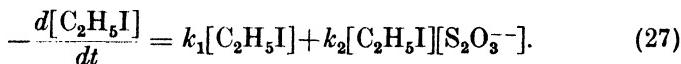
In aqueous solution the rate of attack of the  $\alpha$ -brompropionate ion by the thiosulphate ion resembles closely the rate of the corresponding bromacetate-thiosulphate reaction in its response to ionic environment. With the  $\beta$ -brompropionate ion, surprisingly enough, the salt effect appeared to be in the reverse direction.<sup>†</sup> Moreover, the rate of variation of the apparent energy of activation with temperature, instead of being negative as required by equation (21), was found to be positive and of a higher order of magnitude.<sup>‡</sup> A similar

<sup>†</sup> La Mer and Kamner, *J. Amer. Chem. Soc.*, **53**, 2832, (1931).

<sup>‡</sup> La Mer, *ibid.*, **55**, 1739, (1933).

anomaly in the salt effect at constant temperature has been reported for the reaction of the thiosulphate ion with the monobrom-malonate and monobrom-succinate ions.<sup>†</sup> These apparently anomalous results were interpreted by La Mer<sup>‡</sup> in terms of a postulated asymmetry of the electrical field surrounding the charged organic reactant. It has been shown, however, by a rather elaborate mathematical argument<sup>§</sup> that when only one of the ions is spherically symmetrical while the other is prolate spheroidal, the effect of asymmetry will be experimentally undetectable under ordinary observational conditions. While this conclusion rules out the orientation hypothesis as inadmissible, it gives no clue to the real cause of the alleged deviation from the Debye-Hückel rule.

When ethyl iodide is attacked by the thiosulphate ion in aqueous solution, it is found<sup>||</sup> that more ethyl iodide disappears than its equivalent in terms of thiosulphate, and that the ionic replacement is accompanied by hydrolysis of the halide, according to the equation



The side reaction had hitherto been undetected,<sup>††</sup> although the kinetics of the hydrolysis of substituted alkyl halides had been independently established. It seemed, therefore, that the anomalies reported by La Mer are due to failure to detect and allow for the simultaneous attack of the organic ion by the solvent. A re-examination of the  $\beta$ -brompropionate-thiosulphate reaction by Nielsen<sup>††</sup> suffices to show that when allowance is made for the concurrent hydrolytic reaction, in accordance with equation (27), the gradient of the curve  $\ln k/\sqrt{j}$  has in fact the right sign. There is therefore little reason to doubt that when the reaction is more fully investigated, its response to ionic strength will fall in line with the requirements of the theory which has been found to hold in the other cases.

In the later and more precise work of La Mer and his collaborators

<sup>†</sup> Bedford, Mason, and Morrell, *ibid.*, **56**, 280, (1934); Bedford, Austin, and Webb, *ibid.*, **57**, 1408, (1935). The claim by these authors that an investigation by Conant and his collaborators on another type of reaction revealed a contradiction to the Brönsted relation is not well founded, for Conant clearly stated that further work was necessary before his results could be interpreted in terms of the theory.

<sup>‡</sup> *Chem. Rev.*, **10**, 179, (1932).

<sup>§</sup> Sturtevant, *J. Chem. Physics*, **3**, 295, (1935).

<sup>||</sup> Moelwyn-Hughes, *Trans. Chem. Soc.*, **1576**, (1933).

<sup>††</sup> Slator, *ibid.*, 1286, (1904).

<sup>††</sup> *J. Amer. Chem. Soc.*, **58**, 206, (1936).

cited in earlier sections, due allowance has been made for the simultaneous side reaction.

### *The Influence of Viscosity on the Velocity of Ionic Reactions*

Relatively little work has been done on the effect of varying the viscosity of the medium, while all the other factors which may influence the rate of reaction are kept constant. Using aqueous solutions of the chlorides and nitrates of the alkali metals, Howells† has found that the velocity of the reaction between the iodide and persulphate ions increases as we ascend the periodic group from lithium to caesium, and has noted that, at constant ionic strength, the viscosities of the halide solutions follow the reverse order.‡ Although no constancy of  $k_2\eta$  has been established, it is clear that, other things being equal, the rate of reaction is favoured in the more fluid media, as would be expected if the movement of the ions obeyed Stokes's law.

### *Langevin's Theory*

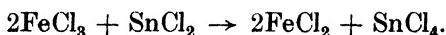
It would be an interesting problem to review the facts dealt with in this chapter in the light of the theory proposed by Langevin to account for the kinetics of ionic reactions in the gaseous phase (p. 253). While such a problem cannot here be pursued far, it may be well to illustrate its nature. Starting from the idea of ionic movement as influenced jointly by the electrostatic and viscous properties of the medium, it can readily be shown, for example, that the sum of the ionic mobilities for a uni-univalent electrolyte at infinite dilution becomes

$$u+v = \frac{Dr^2}{2\pi\epsilon} \left\{ \frac{8\pi kT}{\mu} \right\}^{\frac{1}{2}} e^{\epsilon^2 L/kDr}. \quad (28)$$

To derive corresponding expressions for mobilities in real solutions, however, belongs to another field of inquiry.

### *Ionic Reactions of Higher Kinetic Orders*

Most ionic reactions in solution are bimolecular. Of those which appear to proceed with rates governed by concentrations raised to higher powers, the reduction of ferric chloride by stannous chloride may be mentioned:



† *Trans. Chem. Soc.*, 463, (1939).

‡ Appleby, *Trans. Chem. Soc.*, 97, 2021, (1910).

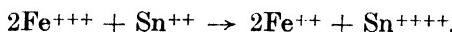
If the initial concentration of ferric chloride be twice that of stannous chloride, the instantaneous rate of reaction after  $t$  seconds is

$$\frac{dx}{dt} = k_3(a-x)^3,$$

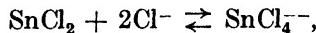
and the termolecular velocity coefficient becomes

$$k_3 = \frac{1}{2t} \left( \frac{1}{(a-x)^2} - \frac{1}{a^2} \right).$$

The approximate constancy of the coefficients thus obtained has long been regarded as evidence that the reaction is in fact a third-order one,† which, on the assumption of complete ionization of the reactants and resultants, may be expressed as follows:



The influence of temperature on the termolecular constant‡ is well summarized by the Arrhenius equation:  $\ln_e k_3 = 36.76 - 21520/RT$ . It is very doubtful, however, whether such a simple mechanism of the reaction can be the true one. van 't Hoff's computation of the order of reaction (p. 48) by various methods§ showed the apparent order,  $n$ , to decrease from 3.22 at an average concentration of 0.08125 gram-ions per litre to 2.37 at a concentration of 0.0375. The value extrapolated to infinite dilution is 1.8, so that the reaction may well be bimolecular.|| Theory predicts for a reaction of this ionic type a very large and positive primary electrolyte effect, and a re-examination of Noyes's results shows that this is in fact the case. Thus, an increase of ionic strength from 0.250 to 0.475 gives a nearly linear increase of rate of about 450 per cent. The primary electrolyte effect alone, however, cannot account for all the features of this familiar analytical reaction. It has been suggested†† that the rate is determined by the interaction of the stannous ion with  $\text{Fe(OH)}_2^+$ . A still more plausible mechanism†† is that a complex ion is first formed between the chloride ion and undissociated stannous chloride,



† Noyes, *Z. physikal. Chem.*, **16**, 546, (1895).

‡ Timofeev, Muchin, and Gurewitsch, *ibid.*, **115**, 161, (1925).

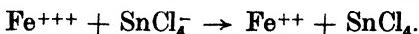
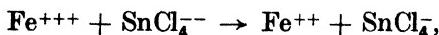
§ *Studies in Chemical Dynamics*, p. 113.

|| *Kinetics of Reactions in Solution*, 1st ed., pp. 37 and 221, (1933).

†† Gorin, *J. Amer. Chem. Soc.*, **58**, 1787, (1936).

†† Weiss, *Trans. Chem. Soc.*, **309**, (1944).

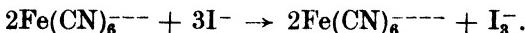
and that the true oxidation then follows in consecutive stages,



Similar explanations may well be necessary for a fuller understanding than we now possess of other ionic reactions which are regarded as termolecular, such as the reduction of silver acetate†



and of the ferricyanide ion‡



The earlier assignment of a fifth order to the latter reaction§ can no longer be credited.

### *The Kinetics of Ionic Reactions in the Gaseous Phase*

The saturation current carried by an ionized gas affords a means of measuring the concentration of ions present in the steady state and the conditions governing their recombination.|| The velocity with which ions combine in the gaseous state at a constant temperature and pressure is found to be bimolecular with respect to the concentration,  $n_i$ , of either kind of ion; hence

$$-\frac{dn_i}{dt} = k_{\text{obs}} n_i^2. \quad (29)$$

The observed bimolecular velocity coefficient is found to be a function of both the temperature and the pressure, but is not very specific for ions produced from simple molecules. A comparison of the absolute rate of reaction with the number of collisions occurring per second in unit volume between uncharged particles at the same concentration, i.e. with

$$Z_{\infty} = n_A n_B r^2 \sqrt{\frac{8\pi kT}{m^*}}, \quad (30)$$

shows that the ions combine under ordinary conditions about 3,000 times more rapidly than would uncharged particles having the same radii. In order to account for the influence of the charges on the frequency of collisions, J. J. Thomson†† introduces the conception of a

† Noyes and Cottle, *Z. physikal. Chem.*, **27**, 578, (1898).

‡ Fräulein von Kise, *Rec. trav. chim. Pays-bas*, **52**, 289, (1933).

§ Donnan and le Rossignol, *Trans. Chem. Soc.*, **83**, 703, (1903).

|| J. J. Thomson and G. P. Thomson, *The Conduction of Electricity through Gases*, 3rd ed., Cambridge, (1928).

†† *Loc. cit.*

radius of capture,  $R$ , which is related as follows to the interionic distance,  $r$ , in the ion pair, of reduced mass  $m^*$ :

$$R^2 = r^2 \left( 1 + \frac{2}{m^* u^2} \int_r^\infty X(r) dr \right). \quad (31)$$

Here  $X(r)$  is the force between the particles, and  $u$  their relative velocity when infinitely far apart. If we introduce Coulomb's expression for the former and the equipartition value for the latter, we have the following relationship between the collision frequency of charged and uncharged particles:

$$Z_{+-} = Z_{00} \left( 1 - \frac{z_A z_B \epsilon^2}{k T r} \right). \quad (32)$$

If the Coulombic force were overwhelming, and no energy of activation were necessary for union, the bimolecular velocity coefficient would then clearly be

$$k_2 = | -z_A z_B | \epsilon^2 r (8\pi/m^* k T)^{1/2}, \quad (33)$$

which, for univalent ions of opposite sign and equal mass,  $m$ , reduces to

$$k_2 = 4\pi r \epsilon^2 / (2\pi m k T)^{1/2}. \quad (34)$$

Similar results emerge from the treatment of ionic reactions in solution, for, by combining equations (6) and III (1), we obtain

$$Z_{+-} = Z_{00} \times P^0 = Z_{00} e^{-z_A z_B \epsilon^2 / k D r},$$

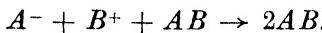
which, on expansion, yields the approximate relation

$$Z_{+-} = Z_{00} \left( 1 - \frac{z_A z_B \epsilon^2 L}{k D r} \right). \quad (35)$$

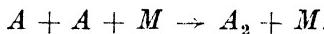
That these interpretations are not correct, however, is indicated by the small values of  $r$  necessitated by their adoption, and by their inadequacy to cope with the dependence of the rate on pressure and temperature.

The order of magnitude of  $k_{\text{obs}}$  at atmospheric pressure and temperature is  $10^{15}$  litres per gram-ion-second. With increasing pressure, the velocity coefficient at constant temperature at first increases in proportion to the pressure; it then either becomes constant or diminishes with a further increase in pressure. When the gaseous concentration is maintained constant, the observed bimolecular velocity constant decreases as the temperature is raised;  $k_{\text{obs}}$  is proportional to  $T^{-n}$ , where  $n$  is 2.5 for air, 2.4 for carbon monoxide, and 2.2 for hydrogen. Most of these features can be explained in terms of the classical theory of J. J. Thomson, the content of which

may be summarized as follows (the reader is referred to his Monograph for the detailed derivations). It is clear from the proportionality of  $k_{\text{obs}}$  to the total pressure that the rate of reaction is governed by ternary collisions, involving two ions and one neutral molecule. The mechanism of the recombination is thus



Although the union of the ions is strongly exothermic, it cannot take place without the presence of a third body to stabilize the union. Precisely the same mechanism governs the union of atoms in the gaseous state: the presence of a molecule,  $M$ , or a third atom, is essential for the combination:



It therefore becomes necessary to estimate the probability of the presence of the third body in a binary collision. Starting with equation (30) for the frequency of binary collisions, the chance that a neutral molecule shall be present at the collision may be taken as the ratio of the volume,  $\frac{4}{3}\pi r^3$ , of the sphere of capture to the average volume,  $v$ , of the neutral molecule. For the latter volume we have the kinetic theory value of

$$v = \sqrt{2\pi r^2 \lambda}, \quad (36)$$

where  $\lambda$  is the mean free path. The probability sought is thus  $2\sqrt{2}r/3\lambda$ , and the number of collisions, per c.c. per second, between the ions at which a neutral molecule is present is therefore

$$\frac{8n_A n_B r^3}{3\lambda} \sqrt{\frac{\pi kT}{m^*}}.$$

The distance,  $r$ , apart of the ions has an average value given by the balancing of the kinetic energy of repulsion and the Coulomb energy of attraction, which, for a pair of univalent and oppositely charged ions is

$$r = \frac{\epsilon^2}{kT}. \quad (37)$$

If each such encounter results in the neutralization of the charges, then

$$-\frac{dn_i}{dt} = \frac{8n_i^2}{3\lambda} \left(\frac{\epsilon^2}{kT}\right)^3 \left(\frac{\pi kT}{m^*}\right)^{\frac{1}{2}}$$

and consequently  $k_{\text{obs}} = \frac{8}{3\lambda} \left(\frac{\epsilon^2}{kT}\right)^3 \left(\frac{\pi kT}{m^*}\right)^{\frac{1}{2}}$ . (38)

According to this equation,  $k_{\text{obs}}$  is seen to be proportional to  $T^{-2.5}$  at a constant pressure; and, at a constant temperature, it is directly

proportional, through  $\lambda$ , to the concentration,  $n$ , of neutral molecules. The essence of the classical interpretation is that the rate of union of ions is a bimolecular process, greatly augmented by the action of interionic attraction, and considerably impeded by the necessity for the presence of a third partner.

The facts may be viewed from another angle† by regarding the union of the ions to form a complex as a ternary process. The complex may then decompose into its constituents unimolecularly or be converted into neutral molecules in a bimolecular collision with ordinary molecules. Denoting the concentrations of ions, ordinary molecules, and complex by  $n_i$ ,  $(n - n_i)$ , and  $n_x$ , respectively, we thus have

$$+\frac{dn_x}{dt} = k_3 n_i^2 (n - n_i) - k_2 n_x (n - n_i) - k_1 n_x,$$

giving the following expression for the concentration of complex molecules in the steady state:

$$n_x = \frac{k_3 n_i^2 (n - n_i)}{k_2 (n - n_i) + k_1}.$$

The rate of neutralization of the charges is consequently (cf. equation I(46))

$$-\frac{dn_i}{dt} = k_1 n_x = \frac{k_1 k_3 n_i^2 (n - n_i)}{k_2 (n - n_i) + k_1}. \quad (39)$$

At relatively low pressures, the reaction is seen to be essentially a termolecular one:

$$-\frac{dn_i}{dt} = k_3 n_i^2 (n - n_i). \quad (40)$$

At high pressures, the reaction proceeds by an apparently bimolecular mechanism:

$$-\frac{dn_i}{dt} = \frac{k_1 k_3 n_i^2}{k_2}. \quad (41)$$

Under the former conditions, which hold when the pressure does not exceed one atmosphere, we see, by comparing equations (29) and (41) that

$$k_{\text{obs}} = k_1 k_3 / k_2. \quad (42)$$

We may now seek to evaluate the absolute magnitude of the termolecular velocity coefficient,  $k_3$ , on the supposition that the rate of reaction is simply the rate at which two ions of opposite sign and one molecule collide. Denoting the standard collision frequency by  $Z_{+0-}$ , we have

$$k_3 = Z_{+0-}.$$

† Moelwyn-Hughes, *Trans. Faraday Soc.*, **34**, 91, (1938).

Following the treatment given in earlier sections of this chapter, we can also write

$$k_3 = Z_{000} e^{-E_e/kT}, \quad (43)$$

where  $Z_{000}$  is the number of collisions per c.c. per second between three uncharged particles of the same masses and dimensions, and  $E_e$  is the electrostatic energy of the triplet relative to a zero value at infinite separation. From experiments of termolecular gaseous reactions, we content ourselves with the experimental value of  $(3.5 \pm 1.5) \times 10^{-38}$  (c.c./molecule)<sup>2</sup>-sec.<sup>-1</sup> for  $Z_{000}$ . To evaluate the term  $E_e$ , it is first necessary to map the energy contour of the three-particle system, taking into account the intrinsic repulsion as well as the Coulomb terms and other energy contributions. When this is done, it is found that, at the distances which matter, the principal term in  $E_e$  is not the attraction between the charged particles, but the energy of induction between the two ions and the uncharged molecule. Denoting the distance between the centre of one ion and the centre of the molecule by  $r$ , the induction energy is  $-2(\frac{1}{2}\alpha\epsilon^2/r^4)$ , where  $\alpha$  is the molecular polarizability. These considerations have been quantitatively applied to the case of the union of ions formed from carbon monoxide. The distance apart of the partners in the complex may be taken as twice the separation (1.15 Å.) of the carbon and oxygen atoms in the molecule: hence  $r = 2.30$  Å. With  $\alpha = 1.35 \times 10^{-24}$  c.c./molecule,  $E_e$  becomes -15,920 calories per gram mole, and, at 25° C.,  $\exp(-E_e/RT)$  is  $4.5 \times 10^{11}$ . The computed value of  $k_3$  is thus  $(1.5 \pm 0.6) \times 10^{-26}$ , which compares favourably with the experimental values (Table 9).

Table 9

*A Comparison of the Termolecular Velocity Coefficients for the Union of three Uncharged Particles with that for the Union of Oppositely Charged Ions and one Uncharged Particle*

Reactants	$k_3$ (c.c./molecule) <sup>2</sup> -sec. <sup>-1</sup>
2NO + O <sub>2</sub>	$2.01 \times 10^{-38}$
2NO + Br <sub>2</sub>	$4.92 \times 10^{-38}$
Ionized CO (CO <sup>+</sup> , CO, CO <sup>-</sup> )	$3.82 \times 10^{-26}$
„ air	$6.89 \times 10^{-26}$
„ CO <sub>2</sub>	$6.63 \times 10^{-26}$
„ N <sub>2</sub> O	$6.30 \times 10^{-26}$
„ SO <sub>2</sub>	$6.30 \times 10^{-26}$

An interesting point arises in any attempt to express  $k_{obs}$  as a function of temperature. We have seen that  $k_{obs}$  can be written as

proportional to  $T$  raised to a small negative power. There can be no objection to treating  $k_{\text{obs}}$  like any other velocity constant by means of the equation of Arrhenius. If we do so, we find that the equation

$$E_A = 1400 - 10T \quad (44)$$

summarizes the facts equally well, over a temperature range of more than  $300^\circ$ . The apparent energy of activation at ordinary temperatures is thus negative; but we must not forget the word 'apparent', for, by equation (42),  $E_A$  consists of at least three terms, one of which, according to equation (43), is further resolvable.

The advantages of the classical theory are its obvious simplicity and its ability to eliminate any specific factors. Its drawback is that it does not account for the high-pressure phenomena, unless an elaborate dependence of the mean free path (equation (38)) can be formulated. The later theory satisfactorily explains the transition in apparent order of reaction, but introduces specificity by the inclusion of molecular polarizabilities. It is, however, precisely because the problem is a difficult one that we should regard it from as many angles as possible.

## V

## REACTIONS BETWEEN IONS AND POLAR MOLECULES

WE have seen in our general survey (Chapter III) that most bimolecular reactions proceeding with normal velocities ( $P \doteq 1$ ) are those between an ion and a polar molecule. It is also true that most reactions between ions and polar molecules have normal velocities. The outstanding exceptions are the saponification of esters by the hydroxyl ion, the rates of which are considerably lower ( $P \doteq 10^{-4}$ ) than those calculated from the simple collision formula, taking the Arrhenius energy of activation as the true value. In dealing with reactions taking place between two charged particles, we saw (Chapter IV) that considerable uniformity emerges from the experimental findings when allowance is made for the electrostatic contribution to the energy of activation. The very abundant material available on the kinetics of reactions between ions and polar molecules may also be examined from the same standpoint, by comparing the observed velocities with those given by the equation

$$k_2 = Ze^{-(E+E_e)/RT} = \frac{N_0}{1000} r^2 \left( 8\pi kT \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right)^{\frac{1}{2}} e^{-(E+E_e)/RT}. \quad \text{IV (3)}$$

It is not quite so easy in the present instance to derive an explicit value for the electrostatic energy,  $E_e$ , under all circumstances. When, however, data can be extrapolated to infinite dilution, the term reduces to

$$\frac{E_e^0}{N_0} = \frac{z_B \epsilon \mu_A \cos \theta}{Dr^2}, \quad (1)$$

as shown on p. 84. Proceeding as in the preceding chapter, we then find that the apparent energy of activation at infinite dilution is related as follows to the true energy

$$E_A^0 = E + \frac{1}{2} RT - (LT-1) \frac{N_0 z_B \epsilon \mu_A \cos \theta}{Dr^2}, \quad (2)$$

and that the ratio of the Arrhenius constant,  $A$ , to the collision frequency,  $Z$ , is

$$P^0 = e^{-Lz_B \epsilon \mu_A \cos \theta / Dr^2 k}. \quad (3)$$

Both terms are seen to depend, not only on the charge,  $z_B \epsilon$ , of the attacking ion and the moment,  $\mu_A$ , of the molecule attacked, but on the angle of approach, relative to the polar axis. Allowing  $\theta$  any value from 0 to  $90^\circ$ , and taking  $r$  as  $3 \times 10^{-8}$  cm., we compute the

ranges in  $P^0$  shown in Table 1. Most of the very numerous reactions between elementary ions and substituted aliphatic compounds in

*Table 1*

*Computed Values of  $P^0$  ( $= A/Z$ ) at 293.1° K. for Reactions between Ions and Polar Molecules, taking  $r$  as  $3 \times 10^{-8}$  cm. and  $\mu$  as 1 Debye unit in Various Solvents*

Solvent	$z_B$	Range of $P^0$ values
$H_2O$	$\pm 1$	0.80–1.25
	$\pm 2$	0.64–1.56
$C_2H_5OH$	$\pm 1$	0.39–2.53
	$\pm 2$	0.16–6.42
$(CH_3)_2CO$	$\pm 1$	0.56–1.78
	$\pm 2$	0.32–3.17

alcoholic solutions fall within this fairly narrow range, which can, of course, be extended by using other values of  $z_B$ ,  $r$ ,  $\theta$ ,  $\mu_A$ ,  $D$ , and  $T$ .

By differentiating equation (2) with respect to temperature, we can estimate the electrostatic contribution to the temperature variation of the apparent energy of activation. Assuming that  $E$  is constant, we have

$$\frac{dE_A^0}{dT} = - \frac{N_0 L^2 T z_B \epsilon \mu_A \cos \theta}{Dr^2}. \quad (4)$$

Let us apply this formula to a reaction between a polar molecule of moment 1.5 Debye units, and a univalent ion ( $z_B = \pm 1$ ) in ethyl alcohol ( $L = 6.02 \times 10^{-3}$ ) at 50° C. ( $D = 21.4$ ). Taking  $r$  to be 3 Å., and allowing for all possible angles of approach ( $\theta = 0$  to  $2\pi$ ),  $dE_A^0/dT$  should lie within the limits of +2.65 and –2.65 calories per gram molecule per degree. These values are too low to be detected by ordinary methods of analysis (cf. an observed accuracy of  $\pm 6.9$  given on p. 61), and are consistent with the constancy of  $E_A$  calculated from the original results of Hecht, Conrad, and Brückner,† and from the careful repetition of Gibson, Fawcett, and Perrin.‡

Just as in the study of reactions between ions, methods arise for determining the distance,  $r$ , from kinetic measurements, so in the study of reactions between ions and dipoles it is possible to estimate the angle  $\theta$ . With the details of the method§ we shall not here be concerned. Some results are shown in Table 2.

† *Z. physikal. Chem.*, **4**, 273, (1889).

‡ *Proc. Roy. Soc., A*, **150**, 223, (1935).

§ *Ibid.*, **157**, 667, (1936).

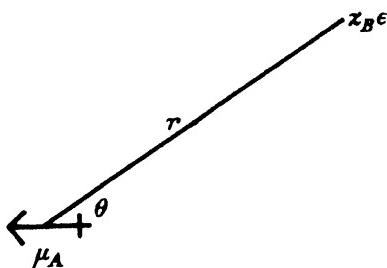
Table 2

Estimation of the Angle of Approach of Ions to Polar Molecules

Reference	Reacting molecule	$\mu_A \times 10^{18}$	Reacting ion	$z_B$	$\cos \theta$	$\theta$
(1)	Ethyl iodide	1.65	<i>m</i> -4-xylyloxyde	-1	0.719	44°
(2)	Ethyl bromide	1.81	Hydroxide	-1	0.819	35°
(3)	Methyl iodide	1.51	Ethoxide	-1	0.602	53°
(4)	1:2-Dinitrobenzene	6.00	Ethoxide	-1	0	90°
(5)	Butyl iodide	1.76	Silver	+1	1.0	0°

(1) Hardwick, *Trans. Chem. Soc.*, 141, (1935).(2) Grant and Hinshelwood, *ibid.*, 258, (1933).(3) Hecht, Conrad, and Brückner, *Z. physikal. Chem.*, 3, 450, (1889).(4) Steger, *ibid.*, 49, 329, (1904).(5) Burke and Donnan, *Trans. Chem. Soc.*, 85, 555, (1904); Pierce and Weigle, *J. Amer. Chem. Soc.*, 48, 243, (1912).

For reactions (1), (2), and (3), which are dynamically the simplest, there is found an average value of 0.71 for  $\cos \theta$ ; the negative ion thus approaches the positive end of the dipole (Fig. 1). In reaction (5), which is unfortunately complicated by heterogeneous catalysis due to one of the products,† the positive ion approaches the negative end of the dipole. Generally, therefore,



ions approach reactant molecules from electrostatically favourable directions. Such is not always the case. There is evidence, for example, that the chloride ion attacking the sulphur monochloride molecule does so against the field of the dipole, that is, the negative ion approaches the negative end of the dipole.‡ Moreover, if the treatment underlying Table 2 is correct, the ethoxide ion attacks the highly polar aromatic compound at right angles to the direction of field exerted by the dipoles of the substituent groups.

FIG. 1.

No real objections have been raised against these conclusions, which seem, on the whole, to be not unreasonable ones. They are subject, however, to the many limitations, experimental and theoretical, of the problem. Even the relatively simple reaction (2) is attended by the unavoidable production of ethylene, for which, in the results

† Senter, *Trans. Chem. Soc.*, 97, 346, (1910).‡ Spong, *ibid.*, 1283, (1934).

discussed, no allowance has been made. In reaction (4) we have omitted the reversibility, and in reaction (5) the heterogeneous catalysis already mentioned. Moreover, the theory on which the calculations are based is at best only an approximation. In order to develop the subject systematically and firmly, we must now pay closer attention, first to some further experimental results, and later to the most promising of the theories.

### *The Energies of Activation of Homologous Reactions*

The most noteworthy feature of homologous bimolecular reactions between ions and polar molecules, in which the ion is common to all reactants and the polar molecules differ by successive structural units of  $-\text{CH}_2-$ , is the approximate constancy of the energy of activation. The regularity holds not only when  $P$  is unity, as in etherification in alcoholic solution,<sup>†</sup> but when  $P$  has much smaller values, as in ester saponification in water<sup>‡</sup> and Finkelstein reactions in acetone.<sup>§</sup> Illustrative examples selected from the earlier data are given in Tables 3 and 4, from the first of which is discernible a tendency in  $E_A$  to alternate rises and falls during the ascent of the series.<sup>||</sup>

*Table 3*  
*Homologous Reactions in Alcoholic Solution*

R	RI + $\text{C}_6\text{H}_5\text{ONa}$			RI + $\text{C}_6\text{H}_5\text{CH}_3\text{ONa}$		
	$k_{42^\circ\text{C}} \times 10^6$	$E_A$	$A \times 10^{-11}$	$k_{50^\circ\text{C}} \times 10^6$	$E_A$	$A \times 10^{-11}$
$\text{CH}_3$	101	22,120	22.1	266	20,570	20.65
$\text{C}_2\text{H}_5$	22.5	22,000	4.00	23.70	21,860	15.67
$\text{C}_3\text{H}_7$	8.67	22,450	3.45	9.24	21,730	4.86
$\text{C}_4\text{H}_9$	8.08	22,090	1.65	6.69	21,560	2.92
$\text{C}_7\text{H}_{15}$	7.52	22,230	0.96	6.68	21,510	2.48
$\text{C}_8\text{H}_{17}$	7.23	22,500	1.37	6.68	21,450	2.21
$\text{C}_{16}\text{H}_{33}$	7.15	22,430	1.93	6.90	21,090	1.26
<i>iso-C<sub>3</sub>H<sub>7</sub></i>	7.58	22,100	2.88	5.52	21,410	1.75
<i>iso-C<sub>4</sub>H<sub>9</sub></i>	3.22	21,790	2.31	8.68	21,350	2.45
<i>iso-C<sub>6</sub>H<sub>11</sub></i>	4.75	22,250	1.56	3.39	21,410	1.07
<i>sec.-C<sub>4</sub>H<sub>13</sub></i>	7.22	22,190	0.41	9.61	21,580	4.01
<i>sec.-C<sub>6</sub>H<sub>17</sub></i>	6.85	22,110	1.28	7.25	21,450	2.40
<i>tert.-C<sub>4</sub>H<sub>9</sub></i>	202	23,320	285	—	—	—

<sup>†</sup> Segaller, *Trans. Chem. Soc.*, **103**, 1421, (1913); *ibid.*, **105**, 106, (1914); Haywood, *ibid.*, **121**, 1904, (1922).

<sup>‡</sup> L. Smith and Olsson, *Z. physikal. Chem.*, **118**, 99, (1925).

<sup>§</sup> Conant and Hussey, *J. Amer. Chem. Soc.*, **47**, 476, (1925).

<sup>||</sup> Indications of this saw-tooth rule were brought to my attention in a private communication by Dr. J. C. Smith.

Greater accuracy of measurement must be achieved, however, before such a regularity can be established. The limits within which  $E_A$

Table 4

$\text{CH}_3\text{COOR} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{ROH}$ in aqueous solution				$\text{RCl} + \text{I}^- \rightarrow \text{RI} + \text{Cl}^-$ in acetone solution		
R	$k_{20^\circ\text{C.}} \times 10^2$	$E_A$	$A \times 10^{-7}$	R	$E_A$	$A \times 10^{-8}$
$\text{C}_2\text{H}_5$	6.78	11,210	1.66	$\text{C}_3\text{H}_7$	18,610	1.2
$\text{C}_3\text{H}_7$	7.05	11,320	2.09	$\text{C}_4\text{H}_9$	19,610	5.0
<i>iso-C<sub>3</sub>H<sub>7</sub></i>	2.10	11,440	0.64	$\text{C}_5\text{H}_{11}$	18,370	1.0
$\text{C}_4\text{H}_9$	6.55	11,370	2.13	$\text{C}_6\text{H}_{13}$	18,620	1.6
<i>iso-C<sub>4</sub>H<sub>9</sub></i>	6.90	11,620	3.00	$\text{C}_7\text{H}_{15}$	18,990	2.6
<i>sec.-C<sub>4</sub>H<sub>9</sub></i>	1.36	11,020	0.24	$\text{C}_8\text{H}_{17}$	18,850	2.0
<i>tert.-C<sub>4</sub>H<sub>9</sub></i>	0.135	13,040	0.78	$\text{C}_{14}\text{H}_{29}$	19,060	2.6
<i>iso-C<sub>6</sub>H<sub>11</sub></i>	6.02	11,040	1.07	$\text{C}_{16}\text{H}_{33}$	19,040	2.0

may be regarded as constant for certain series of homologous reactions are indicated in Table 5: these are not the limits of accuracy of experiments on a single reaction.

Table 5

*Average Energies of Activation ( $E_A$ ) for Certain Homologous Reactions*

Reaction	Solvent	Temperature Range ( $^\circ\text{C.}$ )	$E_A$ (calories/gm. mole)
$\text{ROOC} \cdot \text{CH}_3 + \text{OH}^-$	$\text{H}_2\text{O}$	40	$12,300 \pm 300$
$\text{ROOC} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3 + \text{OH}^-$	$\text{H}_2\text{O}$	40†	$12,720 \pm 150$
$\text{ROOC} \cdot \text{CH}_3 + \text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	30	$16,880 \pm 50$
$\text{RCl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	10	$18,900 \pm 300$
$\text{RCONH}_3 + \text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	40	$19,200 \pm 300$
$\text{RI} + \text{C}_2\text{H}_5\text{O}^-$	$\text{C}_2\text{H}_5\text{OH}$	30	$19,950 \pm 700$
$\text{RI} + \text{C}_6\text{H}_5\text{CH}_2\text{O}^-$	$\text{C}_2\text{H}_5\text{OH}$	30	$21,500 \pm 400$
$\text{RI} + \text{C}_6\text{H}_5\text{O}^-$	$\text{C}_2\text{H}_5\text{OH}$	50	$22,200 \pm 350$

† Schjanberg, *Z. physikal. Chem.*, A, 174, 465, (1935).

*Concomitant Chemical Changes Associated with Reactions between Ions and Polar Molecules*

Nature seems reluctant to let any reaction have it all its own way (p. 16). Let us suppose, for example, that we wished to measure the velocity of the following reaction:

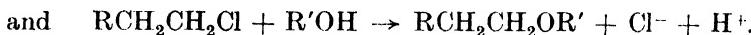


We would, if we followed it carefully, find that it does not proceed

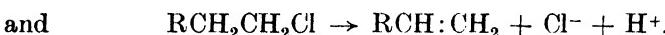
to completion, but to an equilibrium position. It is, in other words, opposed by the simultaneous reaction



In a hydroxylic medium, R'OH, we would also find that both halides react with the solvent, according to the schemes



Many reactions of this type have been examined,<sup>†</sup> and have been found to proceed at a relatively slow rate according to the pseudo-unimolecular mechanism (p. 36). Nor is this all. Alkyl halides on prolonged heating give olefins and hydrogen halides, which, in hydroxylic solvents are largely ionized, so that further complicating reactions are



Decompositions of this kind are known to be facilitated by the presence of hydroxyl ions.<sup>‡</sup> Of very few reactions between ions and polar molecules can it be said that all these disturbances have been taken into account. A good example is afforded by the work of Hughes, Ingold, and Shapiro<sup>§</sup> on the reaction between isopropyl bromide and the hydroxyl ion in '80 per cent.' aqueous alcoholic solution, in which the reverse reaction appears to be absent.<sup>||</sup> Their findings for the principal reaction and its two subsidiaries may be summarized as follows:

Reaction	<i>A</i>	<i>E<sub>A</sub></i>
1. $\beta\text{C}_3\text{H}_7\text{Br} + \text{OH}^- \rightarrow \beta\text{C}_3\text{H}_7\text{OH} + \text{Br}^-$	$1.39 \times 10^{10}$	21,700
2. $\beta\text{C}_3\text{H}_7\text{Br} + \text{OH}^- \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} + \text{Br}^-$	$8.20 \times 10^{10}$	22,640
3. $\beta\text{C}_3\text{H}_7\text{Br} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} \rightarrow \left\{ \begin{array}{l} \beta\text{C}_3\text{H}_7\text{OH} \\ \beta\text{C}_3\text{H}_7\text{OC}_2\text{H}_5 \end{array} \right\} + \text{H}^+ + \text{Br}^-$	$6.52 \times 10^9$	23,160

As these figures show, quite a high percentage of the interaction between the organic halide and the hydroxyl ion results in the elimination reaction (2), which has been established as a bimolecular

† Olivier, *Rec. trav. chim. Pays-bas*, **42**, 516, 775, (1923).

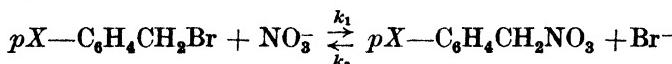
‡ Brusoff, *Z. physikal. Chem.*, **34**, 129, (1900).

§ *Trans. Chem. Soc.*, 225, (1936).

|| See also W. Taylor, *ibid.*, **343**, (1938); Dawson and Pycock, *ibid.*, **778**, (1934).

process. If we choose conditions of temperature and solvent composition so that no reaction with the solvent takes place, the bimolecular velocity coefficient determined by estimations of the rate of decrease in alkalinity or increase in ionic bromide is a composite one, giving the net rate of reaction between the halide and the hydroxyl ion. The results of Hinshelwood and Grant† on the reaction of ethyl halides with potassium hydroxide in ethylalcoholic solution are of this kind. It is clear, however, that their relevance to the collision theory is in no way influenced by the more detailed findings discussed here, which extend the earlier conclusions and, in so far as we can allow for the difference between isopropyl bromide in a mixed solvent and ethyl bromide in a pure one, confirm them. The value of  $A$  found by Hughes, Ingold, and Shapiro‡ for reaction (3) also compares favourably with the value of  $1.5 \times 10^9$  measured for the reaction of ethyl iodide with water.§ In view of the complicated nature of the total reaction and of the limited temperature range covered, no significance can be attached to the differences in the three values of  $E_A$  cited above.

As an illustration of the reversibility met with in reactions between ions and polar molecules, we may examine the data of Baker and Nathan|| on the bimolecular reactions



in pure acetone, which have been recalculated, yielding the constants shown in Table 6. The investigators conclude that, within the limits

*Table 6*

*Arrhenius Constants for Certain Reversible Reactions in Acetone Solution*

<i>X</i>	$E_1$	$E_2$	$E$	$\log A_1$	$\log A_2$
$\text{CH}_3$	17,500	16,850	$17,180 \pm 330$	8.85	9.60
H	18,020	18,380	$18,200 \pm 180$	9.35	10.10
NO	18,740	22,220	$19,480 \pm 740$	10.53	11.54

of accuracy of the work, the equilibrium constants are independent of temperature, so that the apparent energies of activation of the direct and reverse changes are equal. Changes in the rate from one reaction to another are attributed to changes in  $A$ , for which a

† *Trans. Chem. Soc.*, 258, (1933).

‡ Moelwyn-Hughes, *Trans. Chem. Soc.*, 1576, (1933).

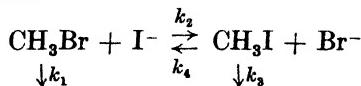
§ *Loc. cit.*

|| *Ibid.*, 236, (1936).

probable reason may be found in the difference between the shapes—spherical and planar, respectively—of the bromine and nitrate ion. This plausible explanation, however, is in no way inconsistent with a concomitant change in  $E$ , which seems to be hinted at in the more detailed analysis of Table 6.

## *Reactions of the Methyl Halides*

A study of the four methyl halides, as prototypes of the numerous alkyl halides, is a fundamental necessity for the development of our subject. They possess the obvious advantage of not being able to form olefins, but their kinetic investigation, despite this, has proved to be by no means straightforward. When, for example, we wish to find the rate of substitution of iodine for bromine in methyl bromide in aqueous solution, we cannot do so without embracing the comprehensive kinetic scheme



The constants,  $k_1$  and  $k_3$ , are known, and by means of chemical analysis and the velocity equations

$$+d[\text{I}^-]/dt = k_3[\text{CH}_3\text{I}] + k_4[\text{CH}_3\text{I}][\text{Br}^-] - k_2[\text{CH}_3\text{Br}][\text{I}^-],$$

$$+d[\text{Br}^-]/dt = k_1[\text{CH}_3\text{Br}] + k_2[\text{CH}_3\text{Br}][\text{I}^-] - k_4[\text{CH}_3\text{I}][\text{Br}^-],$$

the constants  $k_2$  and  $k_4$  may be evaluated.

A summary of the meagre results at present available is given in Table 7. The constancy in  $E_A$  for reaction (1) in two media is to be noted, and the relatively high value of  $A$  in reactions (5), (6), and (8), which must be due, in part, to the double charge of the entrant ion.

Table 7

### *Arrhenius Constants for Reactions of the Methyl Halides in Solution*

Reference	Reaction	Solvent	<i>A</i>	<i>E<sub>A</sub></i>
(1)	$\text{CH}_3\text{Br} + \text{I}^- \rightarrow \text{CH}_3\text{I} + \text{Br}^-$	Water	$1 \cdot 68 \times 10^{10}$	$18,260 \pm 130$
(2)	$\text{CH}_3\text{I} + \text{Br}^- \rightarrow \text{CH}_3\text{Br} + \text{I}^-$	"	$6 \cdot 02 \times 10^6$	$19,310 \pm 750$
(3)	$\text{CH}_3\text{Br} + \text{I}^- \rightarrow \text{CH}_3\text{I} + \text{Br}^-$	Methanol	$2 \cdot 26 \times 10^{10}$	$18,250 \pm 250$
(4)	$\text{CH}_3\text{I} + \text{Br}^- \rightarrow \text{CH}_3\text{Br} + \text{I}^-$	"	$3 \cdot 01 \times 10^{11}$	$21,400 \pm 1,000$
(5)	$\text{CH}_3\text{Cl} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{CH}_3\text{S}_2\text{O}_8^- + \text{Cl}^-$	Water	$1 \cdot 02 \times 10^{12}$	$20,490$
(6)	$\text{CH}_3\text{Br} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{CH}_3\text{S}_2\text{O}_8^- + \text{Br}^-$	"	$5 \cdot 05 \times 10^{12}$	$19,230$
(7)	$\text{CH}_3\text{Br} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{CH}_3\text{S}_2\text{O}_8^- + \text{Br}^-$	"	$6 \cdot 82 \times 10^{12}$	$19,540$
(8)	$\text{CH}_3\text{I} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{CH}_3\text{S}_2\text{O}_8^- + \text{I}^-$	"	$2 \cdot 19 \times 10^{12}$	$18,780$

(1), (2) *Trans. Chem. Soc.*, 204, (1938). (3), (4) *Trans. Faraday Soc.*, 35, 368, (1938). (5), (7), (8) Slator, *Trans. Chem. Soc.*, 85, 1286, (1904). (6) *Trans. Faraday Soc.*, 37, 279, (1941).

### *Experiments on the Effect of Dilution*

The bimolecular velocity coefficient of reactions between alkyl halides and ions in hydroxylic solvents increases as the dilution is increased, often tending to a limiting value at high dilutions which is from two to four times as great as the value found at a concentration of one gram mole per litre. Hecht, Conrad, and Brückner's data for

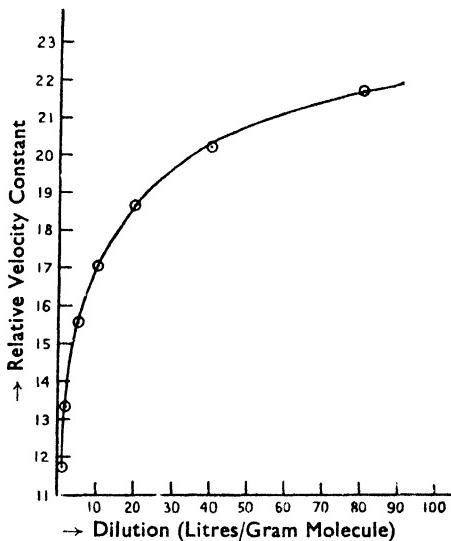


FIG. 2. Reaction between methyl iodide and sodium ethoxide in ethylalcoholic solution at 36° C.

one such reaction are shown in Fig. 2.† This factor, which has not been included in the data summarized in Table I of Chapter III, brings the average value of  $P$  nearer to unity in most cases. Hecht's results are reproduced excellently by means of an empirical equation proposed by him; and, although equations of the same form have been found to apply to data for kindred reactions at atmospheric pressure‡ and to the same reaction under high pressures,§ they are void of any discernible physical content.

The correct interpretation of the influence of dilution has been given by Acree and his collaborators in terms of the dual hypothesis.||

† *Z. physikal. Chem.*, **49**, 329, (1904).

‡ Cox, *Trans. Chem. Soc.*, **113**, 666, (1918); **119**, 143, (1921); **121**, 1904, (1922).

§ Gibson, Fawcett, and Williams, *Proc. Roy. Soc., A*, **150**, 223, (1935).

|| See, for example, Robertson and Acree (*J. Amer. Chem. Soc.*, **37**, 1902, (1915)), where reference to twenty preceding papers of the same series will be found; and Marshall and Acree, *J. Phys. Chem.*, **19**, 589, (1915).

On the assumption that both ions and neutral molecules react, we have

$$k = k_i \alpha + k_m (1 - \alpha), \quad (5)$$

where  $k_i$  and  $k_m$  are the reactivities of the ion and undissociated molecule respectively and  $\alpha$  is the degree of ionization. Writing the equation in the form  $k = k_m + \alpha(k_i - k_m)$ ,

it is seen that  $k_i$  and  $k_m$  can be found by plotting the observed velocity against the degree of dissociation. The curve should be linear, with a slope equal to  $(k_i - k_m)$  and an intercept of  $k_m$ . An equation of this kind accounts satisfactorily for the velocity of reaction between 1-phenyl-thiourazol and ethyl iodide at various dilutions in ethyl-alcoholic solution at 25° C.†

When the dual hypothesis was being developed by Acree and his collaborators, less satisfactory methods were known than are now available for determining the degree of dissociation from electrical conductances. This circumstance, and partly the relatively high concentrations employed, led to low values of about 2 to 3 for the ratio  $k_i/k_m$ . The true value is known from other kinetic sources to have the order of magnitude  $10^{3\pm 1}$ . It is gratifying that the hypothesis, which is essentially a sound one, should have been given such a thorough re-examination according to later standards.

J. A. Mitchell,‡ in a study of the interaction of sodium guaiacoxide with numerous straight-chained alkyl iodides, finds  $k_m$  to be negligibly small. Under the conditions of his experiments, therefore, only the ion reacts with the alkyl halides. A specimen of his results, shown in Table 8, refers to ethyl iodide, kept at a constant concentration of 0.24 moles per litre and a constant temperature of 55° C. The dilution effect here appears to be entirely exerted on the ionization of the base, and thus only indirectly on the kinetics of the reaction between the halide molecule and the ion. On combining the average value of the bimolecular constant with the similar results obtained at other temperatures, we obtain, for this reaction,

$$k = 6.34 \times 10^{11} \times e^{-20590/RT}$$

Mitchell finds the values of  $P$  for the family of reactions to lie within the limits of 0.04 and 2.96. Similar conclusions are drawn by Woolf§ from his results on the dilution effect, using sodium eugenoxide and

† Chandler and Acree, *Z. physikal. Chem.*, **91**, 607, (1916).

‡ *Trans. Chem. Soc.*, 1792, (1937).

§ *Ibid.*, 1172, (1937).

Table 8

*The Influence of Dilution on the reaction between Ethyl Iodide (0.24 M) and Sodium Guaiacoxide in Ethylalcoholic Solution at 55° C. (Mitchell)*

Concentration of base (mole/l.)	$\alpha$	$k \times 10^4$ (litre/gm. mol.-sec.)	$(k/\alpha) \times 10^3$
0.24	0.0600	7.65	1.275
0.22	0.0622	7.82	1.257
0.20	0.0648	8.03	1.240
0.17	0.0697	8.42	1.208
0.14	0.0753	9.07	1.204
0.12	0.0801	9.68	1.209
0.10	0.0855	10.50	1.232
0.08	0.0938	11.60	1.233
0.06	0.1065	13.20	1.241
0.04	0.1266	15.59	1.260
Average 1.239			

a variety of alkyl iodides. In the case of propyl iodide, the solution of several pairs of equations gives the mean results  $k_i = 1.90$  and  $k_m = -0.001$  at 75°. The interpretation is, of course, not that  $k_m$  has a negative value, but that it is too small to be measured by the method and under the experimental conditions used. The ratio,  $P$ , for Woolf's reactions has an average value of 1.5, the highest figure found being 3.6. Still more extensive data relating to *m*-4-xylyloxide† consolidate the position.

We see, then, that the bimolecular velocity coefficient, reckoned on the concentration of the reactive ion rather than on the total concentration of base, is independent of the dilution. Further examples of this effect, taken from earlier work, are summarized in Table 9. The limits assigned to Burgarsky's figures are not experimental errors, but indicate the changes found by using various alkalies. The absence of a salt effect must be regarded as a fairly general one in reactions between ions and polar molecules. When a salt effect does appear, it is often satisfactorily expressed by the empirical relation,‡

$$k = k^0 e^{Gc}, \quad (6)$$

where  $G$  is a constant. There is thus a linear dependence,

$$k = k^0(1 + Gc), \quad (7)$$

when the ionic concentration,  $c$ , is low.

† Hardwick, *Trans. Chem. Soc.*, 141, (1935).

‡ Grube and Schmidt, *Z. physikal. Chem.*, 119, 19, (1926).

Table 9

*The Influence of Dilution on Certain Reactions between Ions and Polar Molecules.*  $k$  is a Bimolecular Coefficient for the first two Reactions, and a pseudo-unimolecular one ( $\text{sec.}^{-1}$ ) for the third Reaction

Dilution of electrolyte (litres/gm. mole)	$\text{o-(NO}_2\text{)}_2\text{C}_6\text{H}_4 + \text{C}_6\text{H}_5\text{O}^-$ in ethyl alcohol† $k_{45^\circ} \times 10^4$	$\text{CH}_3\text{COOC}_6\text{H}_4 + \text{OH}^-$ in water‡ $k_{15^\circ} \times 10^4$	$\text{Cr}[\text{CO}(\text{NH}_3)_6]^{3+} + \text{H}_2\text{O}$ in water§ $k_{15^\circ} \times 10^4$
5	—	—	1.83
10	—	—	1.85
20	3.83	$6.43 \pm 0.22$	1.87
40	3.82	$6.24 \pm 0.22$	1.84
60	3.82	—	—
80	3.83	$6.29 \pm 0.08$	—
100	3.82	6.32	—

† Steger, *Z. physikal. Chem.*, **49**, 320, (1904).

‡ Arrhenius, *ibid.*, **1**, 110, (1887); Burgarsky, *ibid.*, **8**, 398, (1891).

§ Kilpatrick, *J. Amer. Chem. Soc.*, **50**, 359, (1928).

### Theoretical Treatment of the Dilution Effect

It can readily be shown† that the potential,  $V$ , at a distance,  $r$ , from a dipole of moment,  $\mu_A$ , in a medium of dielectric constant,  $D$ , is approximately

$$V = (\mu_A \cos \theta / Dr^2)(1 + \kappa r)e^{-\kappa r}, \quad (8)$$

where  $\kappa$  is defined by equation (7) of Chapter IV. At low ionic concentrations, we have, by expansion,

$$V = (\mu_A \cos \theta / Dr^2)(1 - \kappa^2 r^2), \quad (9)$$

and for the energy of interaction of the dipole with an ion of charge  $z_B \epsilon$  under these conditions,

$$\frac{E_e}{N_0} = \frac{z_B \epsilon \mu_A \cos \theta}{Dr^2} (1 - \kappa^2 r^2), \quad (10)$$

which reduces to equation (1) for solutions of zero ionic strength. According to equation IV (8), we obtain for the bimolecular velocity coefficient the expression

$$k = Ze^{-E/RT} e^{-(z_B \epsilon \mu_A \cos \theta / Dr^2 kT)(1 - \kappa^2 r^2)}, \quad (11)$$

which may also be written in a form more convenient for discussing electrolyte effects at a constant temperature:

$$k = k^0 e^{+z_B \epsilon \mu_A \cos \theta \kappa^2 / DkT}. \quad (12)$$

These relations, it will be noted, are analogous to equations (9), (10),

† Spong, *Trans. Chem. Soc.*, 1283, (1934).

and (11) of Chapter IV. At low ionic concentrations, a linear electrolyte effect is to be expected, for then,

$$k = k^0 \left( 1 + \frac{z_B \epsilon \mu_A \cos \theta \kappa^2}{DkT} \right). \quad (13)$$

More generally, an exponential salt effect must hold, and equation (12) can obviously be written in the form

$$\log_{10} k = \log_{10} k^0 + qj, \quad (14)$$

where  $j$  is the ionic strength, and

$$q = \frac{8\pi N_0 \epsilon^3 z_B \mu_A \cos \theta}{2303(DkT)^2}. \quad (15)$$

It is not contended that these relations† are more than of approximate validity. They are in agreement with the empirically established rule of Grube and Schmid‡ and with later, more elaborate, theoretical treatments.§ Their derivation is much more direct, and, it is believed, physically no less plausible, than the familiar attempts|| based on an assumed linear dependence of the dielectric constant on ionic concentration. The present formulae have the additional advantage of not requiring empirical constants for their test.††

On the basis of the present theory, an increase in ionic concentration causes an increase in the rate of reaction between an ion and a polar molecule when the approach of the ion to the dipole takes place against the repulsion of the field exerted by it. When the encounter is aided by the electrostatic field, the rate is decreased with an increase in electrolyte concentration. The numerous examples of reactions with rates independent of dilution are interpreted as evidence that the ion attacks the dipole at right angles to the direction of its axis, or that the electrostatic effect is less than the error in experiment.

† Moelwyn-Hughes, *Proc. Roy. Soc., A*, **157**, 667, (1936). Equation (42) in the version which I gave in *Acta Physicochim. U.S.S.R.*, **4**, 173, (1936) is in error by a factor of 2.

‡ *Loc. cit.* § e.g. Kirkwood, *J. Chem. Physics*, **24**, 233, (1939).

|| Debye, *Z. physikal. Chem.*, **130**, 56, (1927); Gross, *Monatsh.*, **53**, 445, (1929); Scatchard, *Chem. Rev.*, **10**, 229, (1932); Gross, *Acta Physicochim. U.S.S.R.*, **5**, 583, (1935).

†† Bateman, Church, Hughes, Ingold, and Taher, *Trans. Chem. Soc.*, 983, (1940), unaware of this treatment, have independently developed one with which it is virtually identical. For the dipole moment,  $\mu_A$ , however, they write  $\alpha e d$ , where  $\alpha e$  is the charge at the end of a dipole of length  $d$ , and  $\alpha$  is the fraction of the electronic charge,  $\epsilon$ .

### *Substitution Reactions and the Walden Inversion*

Emil Fischer's dictum that 'the Walden inversion seems to be a general phenomenon which stands in intimate relationship to the nature of substitution processes',† which has, from time to time, been often re-expressed in various forms,‡ has latterly been given precise physicochemical interpretation, due mainly to Polanyi, Olson,

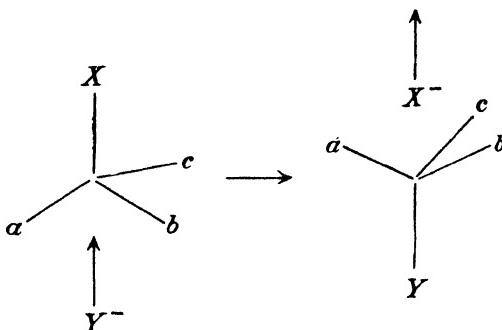


FIG. 3.

and their collaborators.§ The modern theory, so far as one can judge, possesses the hall-marks of truth. Reduced to a minimum, its content may be gauged with reference to substitution processes undergone by the saturated compound  $abcCX$ , in which the dipole has the direction  $\vec{-C-X}$ . When the ion  $Y^-$  which is to be substituted is negatively charged, it is, according to the electrostatic principles dealt with on p. 84, disposed to approach the molecule from the direction indicated in Fig. 3.|| If its advances are successful, it will take a firmer hold of the carbon atom than does ion  $X$ , which is consequently ousted. The exchange of partners is accompanied by the fanning out of the atoms,  $a$ ,  $b$ , and  $c$ , attached to the carbon atom, leading first to a compound of higher symmetry (p. 14), in which atoms  $C$ ,  $a$ ,  $b$ , and  $c$  are coplanar, and eventually to a turning inside-out of the molecule. The substitution should therefore be accompanied by inversion of optical rotatory power. It is possible that the approach is unsuccessful, and that

† *Annalen*, **381**, 123, (1911).

‡ e.g. by Werner, *ibid.*, **386**, 70, (1912), and by Meisenheimer, *ibid.*, **456**, 126, (1927).

§ Meer and Polanyi, *Z. physikal. Chem.*, **B**, **19**, 164, (1932); Bergmann, Polanyi, and Szabo, *ibid.*, **B**, **20**, 161, (1933); *idem*, *Trans. Faraday Soc.*, **32**, 843, (1936); Olson, *J. Chem. Physics*, **1**, 418, (1933); Olson and Long, *J. Amer. Chem. Soc.*, **56**, 1294, (1934).

|| After Meer and Polanyi, *loc. cit.*

ionic attack must be left to the positive ion,  $Z^+$ . In its disengagement of ion  $X$ , no inversion of the molecule takes place (Fig. 4). Most catalyses by hydrogen ion probably belong to this latter category.

From a detailed examination of the work of Szabo<sup>†</sup> we derive the

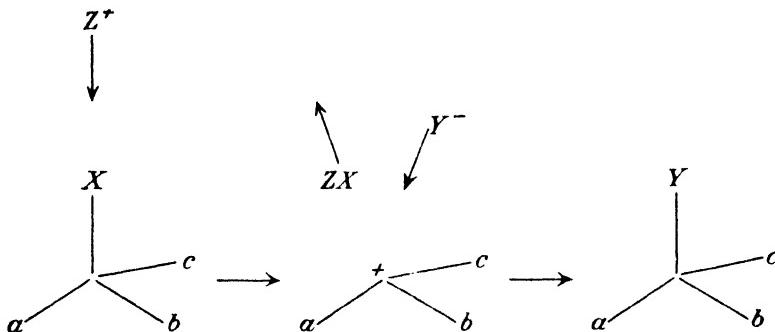


FIG. 4.

following Arrhenius constants for the racemizations investigated by him in acetone solution:

Racemization	$A$	$E_A$
$\text{MeBtHCl} + \text{I}^- \rightarrow \text{ICHBtMe} + \text{I}^-$	$9.9 \times 10^9$	16,500
$\text{MePrHCl} + \text{I}^- \rightarrow \text{ICHPrMe} + \text{I}^-$	$6.5 \times 10^9$	17,300

Me, Pr, and Bt stand for the methyl, normal propyl, and normal butyl groups. The change in optical rotation is a unimolecular one, and proportional to the constant concentration of lithium iodide during a given experiment. The  $A$  values refer to the bimolecular reaction between the ion and the molecules. Though some doubt attaches to the accuracy of these results, due to slight departures from linearity of the  $k_1 - [\text{I}^-]$  curves, particularly at the higher temperatures, and to the unavoidable difficulty of completely drying the solvent, there remains no doubt of their nearness to the results obtained for the rate of the substitution reactions measured by chemical analysis in the same solvent (p. 124). Evidence of a similar nature has been obtained by Olson and Young,<sup>‡</sup> from whose work the data summarized in Table 10 are reproduced. Similar kinetic results have been found<sup>§</sup> for the racemization of certain  $\alpha$ -halogeno-phenylacetic acids.

<sup>†</sup> Über den Mechanismus einfacher Substitutionsreaktionen und die Waldensche Umkehrung, Thomas and Hubert, Berlin, (1933).

<sup>‡</sup> J. Amer. Chem. Soc., 58, 1157, (1936).

<sup>§</sup> Olson and Long, ibid., 58, 383, (1936).

Table 10

*Arrhenius Constants derived from the Bimolecular Velocity Coefficients of Optical Inversions and Racemizations of Certain Halogen-substituted Succinic Acids in Aqueous Solution*

Reaction	$A \times 10^{-10}$	$E_A$
<i>l</i> -Bromsuccinic acid + Br <sup>-</sup>	1.49	21,800 ± 50
<i>l</i> -Chlorsuccinic acid + Cl <sup>-</sup>	0.842	24,770 ± 150
<i>l</i> -Chlorsuccinic acid + Br <sup>-</sup>	0.624	23,540 ± 150
<i>l</i> -Bromsuccinic acid + Cl <sup>-</sup>	3.95	23,650 ± 40

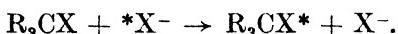
### *Isotopic Tracer Reactions*

More direct proof of the correctness of this theory has resulted from experiments conducted with radioactive atoms as 'tracers'.

The ordinary methods of chemical analysis do not make it possible to follow the rate of the reaction



If the three groups R attached to the carbon atom are different, we can, of course, use the polarimetric method to determine the rate of inversion. On the other hand, if we start with the ordinary compound R<sub>3</sub>CX and with a radioactive salt, KX\*, for example, we have a means of following the change



The methods of chemical analysis, the Geiger counter method of radioactive estimation, and the fact that one of the reactants is volatile while the other is not, together make it possible, in principle, to measure the rate of reaction. It is much easier, however, to select an optically active molecule. The rate of optical inversion is then directly measurable, and separation of the reactants, followed by Geiger counts, yields the rate of substitution. The latter method is the less accurate. Within the estimated limits of experimental uncertainty, the results† leave no room for doubt; the rate of optical inversion is the same as the rate of ionic substitution. The data, which are summarized in Table 11, refer to aqueous acetone at different temperatures, but the exact conditions are irrelevant.

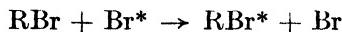
† Hughes, Juliusberger, Scott, Topley, and Weiss, *Trans. Chem. Soc.*, 1173, (1936); Hughes, Juliusberger, Masterman, Topley, and Weiss, *ibid.*, 1525, (1936); Cowdrey, Hughes, Nevell, and C. L. Wilson, *ibid.*, 209, (1938).

Table 11

*A Comparison of the Rates of Optical Inversion and Isotopic Substitution for Certain Reactions between Ions and Dipoles in Aqueous Acetone Solution*

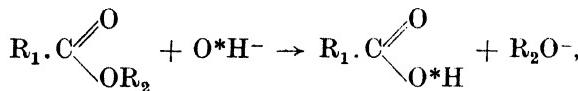
Reaction	$k_{\text{optical inversion}}$	$k_{\text{isotopic substitution}}$
$(\text{CH}_3)(\text{COOH})\text{HCB}\ddot{\text{r}} + \text{Br}^*$	$5.24 \pm 0.05$	$5.15 \pm 0.50$
$(\text{CH}_3)(\text{C}_2\text{H}_5)\text{HCl} + \text{I}^*$	$2.88 \pm 0.03$	$3.00 \pm 0.25$
$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{HCB}\ddot{\text{r}} + \text{Br}^*$	$3.18 \pm 0.05$	$3.49 \pm 0.37$

Sugden and his collaborators† have measured the influence of temperature on the isotopic reactions

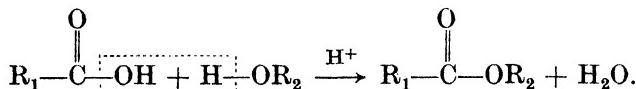


in various hydroxylic media, R being the propyl, isopropyl, butyl, isobutyl or tertiary butyl radical. The values of  $E_A$  range from 18,100 to 22,900 and are accurate to about  $\pm 300$  calories per gram mole. On applying equation (1) of Chapter III, reasonable values are derived for the critical separation ( $r_A + r_B$ ), which, on an average, is found to be  $2.63 \times 10^{-8}$  cm.

The use of radioactive atoms as tracers is becoming increasingly important. By working with water rich in a heavy isotope of oxygen, for example, Polanyi and Szabo‡ showed that the hydroxyl ion, in the saponification of esters, goes in as such,



and thus appears in the acid produced by hydrolysis, and not in the alcohol. Similarly, I. Roberts and Urey§ have proved that acid-catalysed esterification proceeds by the mechanism



In the acid-catalysed hydrolysis of esters, cleavage is in the  $\text{R}_1\text{CO}-\text{OR}_2$  and not in the  $\text{R}_1\text{COO}-\text{R}_2$  link.||

† Elliott and Sugden, *Trans. Chem. Soc.*, 1836, (1939); le Roux, Lu, Sugden, and Thomson, *ibid.*, 586, (1945).

‡ *Trans. Faraday Soc.*, 30, 508, (1934).

§ *J. Amer. Chem. Soc.*, 60, 2391, (1938).

|| Datta, Day, and Ingold, *Trans. Chem. Soc.*, 838, (1939).

### *The Influence of Substituents on the Velocity of Reaction*

The chemist would greatly increase his power if he could foretell the course and velocity of reactions in general. Historically, the organic chemist has been more successful in predicting the type of change likely to take place when two compounds are brought together, while the physical chemist has proved to be more trustworthy in foreseeing the factors likely to determine the rate of chemical change. Too often, alas, has the skill of the organic chemist been regarded as a kind of hunch, incapable of quantitative formulation, and the industry of the physical chemist directed to quantitative measurements of properties without a clear vision as to their ultimate use. Recent years have witnessed a veritable *rapprochement*, for which the study of chemical kinetics in solution is chiefly responsible.

We confine attention here to the effect of substituents on the velocity of reactions between ions and polar molecules, upon which there is a prodigious† and rapidly expanding‡ literature.

The necessity for molecules to acquire a critical energy is, as we have seen, a fairly general condition for the occurrence of chemical change. That molecules should meet is another condition. When these two conditions suffice, the rate of reaction is the rate at which molecules meet with sufficient violence, and the simple collision theory is said to hold. In looking for further conditions which may have to be satisfied, we have found it convenient to classify bimolecular reactions according to the type of electrostatic forces exerted between the participants, and have further shown, in the case of ionic reactions, that due allowance for the effects of a Coulombic force is sufficient to account for what would otherwise be regarded as fantastically high abnormalities. When we enter the field of the effect of substitution on the velocity of chemical change, we can at the outset say that detection of the form and determination of the magnitude of the forces due to the substituent take us more than halfway towards our goal. In drawing this conclusion we are not

† See, for example, Wittig, *Stereochemie*, Leipzig, (1930); Froudenberg, *Stereochemie*, Deuticke, Leipzig and Vienna, (1933); Hückel, *Theoretische Grundlagen der Organischen Chemie*, Leipzig, (1931).

‡ See, for example, Bateman, Carter, Cooper, Church, Cowdrey, Hughes, Ingold, MacNulty, Masterman, Scott, Shapiro, and Taher, *Trans. Chem. Soc.*, pp. 1177-1280, (1937), and pp. 899-1029, (1940). Cf. an earlier account of the influence, in some forty different types of reactions, of substituting the  $\text{--NO}_2$ , the  $\text{--Cl}$ , and the  $\text{--CH}_3$  groups in the *o*-, *m*-, and *p*-position (G. Williams, *Trans. Chem. Soc.*, 37, (1930)) in terms of the version then current of the electronic theory of organic reactions.

dismissing the primitive notion of steric hindrance, such as is bound to obtrude when, for example, we investigate the reactivity of the phenolic hydroxyl group, at both *ortho* positions of which is attached a voluminous radical such as the tertiary butyl group of atoms,† for mechanical obstruction is, of course, simply a manifestation of a repulsive force.

Bradfield and his fellow workers‡ have made a careful analysis of their results on the velocity of nuclear halogenation in compounds of the type  $X-\text{C}_6\text{H}_4-\text{OR}$ , basing their treatment on the slightly modified collision expression for the bimolecular velocity coefficient:

$$k = spZe^{-E/RT}. \quad (16)$$

Here  $Z$  is the usual collision frequency for systems of unit concentration,  $s$  a steric factor affected chiefly by the shape of the molecule, and  $p$  a phase factor determined by periodic disturbances within the molecule. Knowledge of the separate values of  $p$  and  $s$  is not within our reach, but Bradfield found, in the reactions investigated by him, that the product  $ps$  ( $= P$ ) was constant for a wide variety of aromatic ethers. We can then write

$$k = PZe^{-E/RT}, \quad (17)$$

where  $P$  has a common value for the family of reactions. But it is known that  $Z$  is not a very specific term, and that consequently the term  $A$  in the Arrhenius equation

$$k = A\epsilon^{-E_A/RT} \quad \text{I (4)}$$

must also have a common value. When any two reactions have the same value of  $A$ , we can clearly write the ratio of their velocities as follows:

$$k_1/k_2 = e^{-(E_1-E_2)/RT}. \quad (18)$$

The effect of substitution on the velocities of reactions for which  $A$  has a common value is thus due entirely to the change in the energy of activation brought about by the substitution. This point was also scored about the same time by W. Hückel,§ who demonstrated that the relative rates of hydrolysis of the *cis* and *trans* succinates of *isopropylcyclohexanol* at various temperatures could be completely accounted for by a difference in critical energy of some 2,270 calories. Other examples from data cited in this work will not have escaped

† Pearson and Simons, *J. Amer. Chem. Soc.*, **67**, 352, (1945).

‡ Bradfield and B. Jones, *Trans. Chem. Soc.*, 3073, (1928); Bradfield, W. O. Jones, and Spencer, *ibid.*, 2907, (1931).

§ *Berichte*, **61**, 1517, (1928).

the reader's notice: thus, in Slator's reactions (Table 7), the iodide is attacked about 40 times as rapidly as the chloride, while the  $A$  terms differ by no more than a factor of 2. Generally, however, the difference in energies calculated by means of equation (18), in the form

$$E_1 - E_2 = RT \ln(k_2/k_1), \quad (19)$$

exceeds the difference between the directly observed critical increments (Table 12). The second important conclusion of Bradfield and Jones is that the groups X and R contribute additively to the energy of activation.

Table 12

*Differences in Energy of Activation due to the Replacement of the Iodine by the Chlorine Atom (kilocalcs./gm. mole)*

Reaction	$t^\circ \text{ C.}$	$k_{\text{RI}}/k_{\text{RCl}}$	$RT \ln(k_{\text{RI}}/k_{\text{RCl}})$	$E_A(\text{RCl}) - E_A(\text{RI})$
$\text{C}_6\text{H}_5\text{X} + \text{C}_2\text{H}_5\text{O}^-$	24	106.5	2.8	1.0
$\text{C}_2\text{H}_5\text{X} + \text{HO}^-$	80	67.4	2.9	2.0
$\text{CH}_3\text{X} + \text{S}_2\text{O}_3^-$	47	39.3	2.2	1.7
			Average $2.6 \pm 0.4$	Average $1.6 \pm 0.6$

In order to put the first of Bradfield and Jones's conclusions to a rigorous test, we obviously require a family of reactions proceeding with rates which are widely different, so that changes in the energies may be of real significance. The investigations have accordingly been extended in this direction,† and a summary given by B. Jones‡ is reproduced in Table 13. The velocity constants were measured at  $5^\circ$  intervals in the temperature range  $15^\circ$ - $35^\circ \text{ C.}$ , using solutions containing chlorine, aromatic ether, and hydrochloric acid in the molar ratios of 1:3:1.5. The effect of substitution in these reactions is seen, from the constancy of the  $A$  factors, to be due entirely to changes in  $E_A$ . The earlier conclusion is thus excellently confirmed.

When, as in the present instances, the constant  $A$  is independent of the molecular constitution, we can, by differentiating equation I(4), write for the family of reactions

$$\left( \frac{d \log_{10} k}{d E_A} \right)_T = -\frac{1}{2.303RT}. \quad (20)$$

A plot of  $E_A$  against  $\log_{10} k_T$  should thus be linear, with a gradient

† B. Jones, *Trans. Chem. Soc.*, 1831, (1935); 1854, (1936); 1414, (1938); 267, (1941).

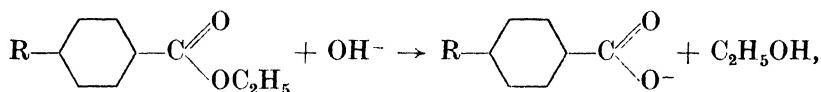
‡ *Ibid.*, 418, (1942).

Table 13

Bimolecular Velocity Coefficients (litres/gm. mole-minute) for the Chlorination of Ethers of the Type  $\text{RO.C}_6\text{H}_4\cdot\text{X}$  in 99 per cent. Acetic Acid

R	X	$k_{20^\circ\text{C.}}$	$E_A$ (calories)	$\log_{10} A$
CHMe <sub>2</sub>	F	9.50	9,850	8.34
Me	O. COPh	7.40	10,100	8.45
CHMe <sub>2</sub>	Cl	5.15	10,500	8.55
Et	Cl	2.33	10,800	8.43
C <sub>6</sub> H <sub>11</sub>	COPh	2.56	10,900	8.55
Et	COPh	2.40	10,950	8.56
Et	CO. C <sub>6</sub> H <sub>4</sub> Cl (p)	1.60	11,050	8.45
CH <sub>2</sub> Ph	F	1.48	11,050	8.42
Me	Cl	1.20	11,350	8.55
CH <sub>2</sub> Ph	Cl	0.786	11,400	8.41
CH <sub>2</sub> . C <sub>6</sub> H <sub>4</sub> Cl (p)	F	0.850	11,450	8.47
CH <sub>2</sub> . C <sub>6</sub> H <sub>4</sub> Cl (p)	Cl	0.467	11,900	8.55
CH <sub>2</sub> . C <sub>6</sub> H <sub>4</sub> . NO <sub>2</sub> (p)	F	0.300	11,950	8.40
CH <sub>2</sub> . C <sub>6</sub> H <sub>4</sub> . NO <sub>2</sub> (p)	Cl	0.182	12,300	8.44
CH <sub>2</sub> . C <sub>6</sub> H <sub>4</sub> . NO <sub>2</sub> (p)	Cl	0.157	12,400	8.45
CH <sub>2</sub> . CO <sub>2</sub> Et	Cl	0.048	12,850	8.28
CH <sub>2</sub> . CO <sub>2</sub> H	Cl	0.049	12,950	8.36
CH <sub>2</sub> . CO <sub>2</sub> Me	Cl	0.046	13,000	8.37
CHMe <sub>2</sub>	NO <sub>2</sub>	0.0141	13,800	8.45
Et	NO <sub>2</sub>	0.0059	14,350	8.48
Me	NO <sub>2</sub>	0.00287	14,650	8.40

of  $-2.303RT$ , as shown in Fig. 5. Another instructive example is afforded by the saponification of *para*-substituted ethyl benzoates



which has been investigated in 85 per cent. ethylalcoholic solution by Ingold and Nathan† and by D. P. Evans, Gordon, and Watson‡ over the respective temperature ranges of 37.5° and 25°. These results (Table 14) also give definite proof that the effect of substitutions in these reactions is entirely due to their influence on the energy of activation. There is also good agreement between the two sets of results, and with velocities previously determined at single temperatures.§

Having proved that the change in velocity is due to a change in energy, we must now seek the way in which this change of energy is brought about.

† *Trans. Chem. Soc.*, 222, (1936).

‡ *Ibid.*, 1430, (1937).

§ McCombie and Scarborough, *ibid.*, 107, 156, (1915); Kindler, *Annalen*, 450, 1, (1926); 452, 90, (1927).

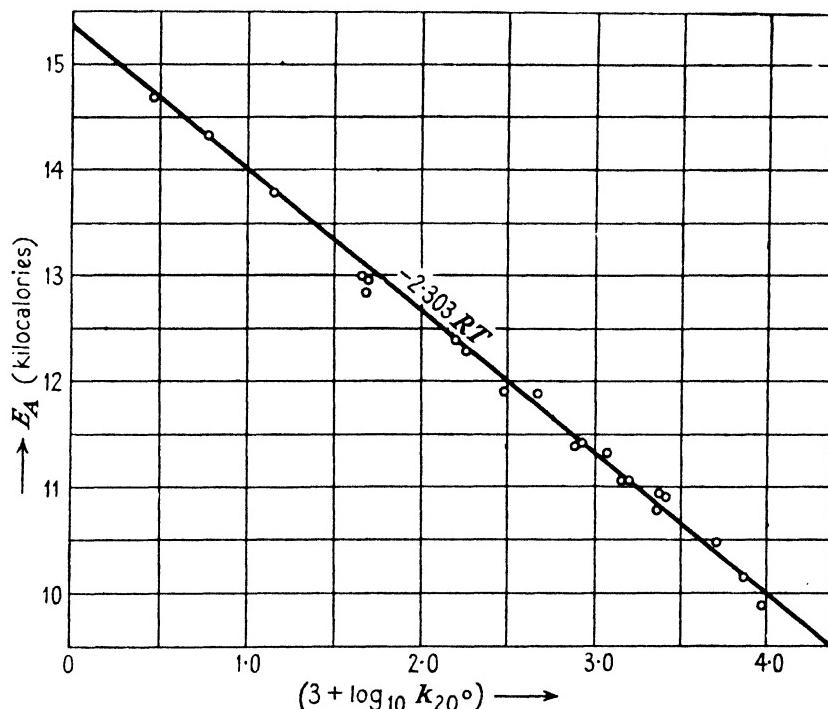
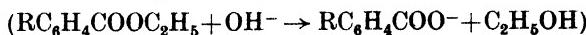


FIG. 5. Arrhenius energies,  $E_A$ , and bimolecular velocity coefficients,  $k$ , for the nuclear chlorination of various phenolic ethers, illustrating the constancy of the term  $A$  for all the reactions (after B. Jones, *Trans. Chem. Soc.*, 419, (1942)).

Table 14

*The Influence of para-substituents on the Energy of Activation of the Saponification of Ethyl Benzoate*

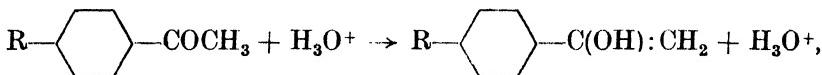


Para-substituent	Investigators	$k_{25^\circ\text{C.}} \times 10^6$	$E_A$	$A \times 10^{-9}$	$\log_{10} A$
NH <sub>2</sub>	I. and N.	1.27	20,000	5.42	9.734
OCH <sub>3</sub>	I. and N.	11.5	18,650	5.38	9.731
CH <sub>3</sub>	I. and N.	25.1	18,200	5.73	9.758
H	I. and N.	55.0	17,700	5.32	9.726
H	E., G., and W.	62.1	17,700	5.80	9.763
F	E., G., and W.	126	17,200	5.13	9.710
Cl	I. and N.	237	16,800	4.93	9.693
I	I. and N.	278	16,700	4.93	9.693
Br	I. and N.	289	16,800	5.82	9.765
NO <sub>2</sub>	I. and N.	5,670	14,500	2.30	9.362
NO <sub>2</sub>	E., G., and W.	7,200	14,800	5.10	9.707

Nathan and Watson† found that the (apparent) energy of activation for a series of similar reactions between a common ion and aromatic molecules into which groups of dipole moment  $\mu$  had been substituted could be represented by an equation of the form

$$E_s = E_u + K_1\mu + K_2\mu^2, \quad (21)$$

where the subscripts refer to substituted and unsubstituted reactants.  $K_1$  and  $K_2$  are constant for a given series, and may have positive or negative values. This relationship is consistent with general electrostatic principles‡ and with the detailed electronic theory of substitutive effects.§ The term  $K_1\mu$  represents the direct effect due to the field exerted, at the point of attack, by the dipole of the substituted group; the term  $K_2\mu^2$  represents a secondary effect due to the polarity induced at the seat of attack by the dipole of the substituted group. The relatively weak induction effect is transmitted from one bond to another, starting at the bond containing the substituted dipole, and finishing up in the bond which is being attacked by the ion.|| Perhaps the only criticism which could be raised concerning the use of equation (21) is the occasional presentation of the induction effect in proportions which appear to be slightly magnified, and not always supported by experiment. One example may be discussed by way of illustration. It refers to the enolization of nuclear-substituted derivatives of acetophenone, e.g.



the rate of which, as we have seen (p. 43), is proportional to the concentrations of ketone and catalyst. The curve in Fig. 6 has been drawn†† so as to pass through three selected points, and is given analytically by the equation

$$E_s = E_u - 429\mu - 53.6\mu^2, \quad (22)$$

according to which  $E_s - E_u$  has a maximum value of about +860

† *Trans. Chem. Soc.*, 890, (1933).

‡ Waters, *ibid.*, 1551, (1933).

§ Ingold, *Chem. Rev.*, 15, 227, (1934); see also R. Robinson, *An Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions*, Institute of Chemistry Lectures, (1932).

|| The mechanism of transmission has been discussed by J. J. Thomson, *Phil. Mag.*, 46, 497, (1923), and by L. E. Sutton, *Proc. Roy. Soc., A*, 133, 668, (1931).

†† D. P. Evans, Morgan, and Watson, *Trans. Chem. Soc.*, 1174, (1935).

calories when  $\mu = 4$  Debye units. The constants are so chosen as to give the energy in calories per gram molecule when  $\mu$ , the dipole moment of the corresponding substituted benzene, is in Debye units (1 Debye unit =  $10^{-18}$  e.s.u.). Deviations from the curve are regarded by the authors as due to experimental error, and they are

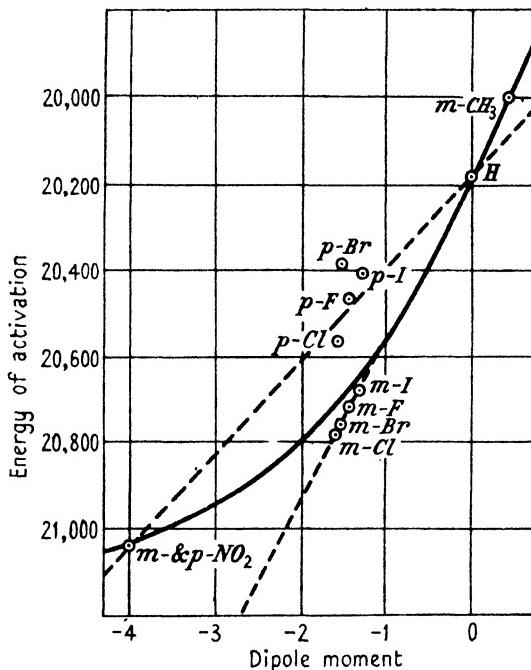


FIG. 6. The effect of *meta*- and *para*-substituents on the apparent energy of activation for the enolization of acetophenone, catalysed by hydrogen ions (after Evans, Morgan, and Watson).

certainly of the right order of magnitude for this to be true. The two broken lines which we have superimposed on the original curve pass, respectively, through the points for *meta*- and *para*-substituted reactants. The only departure now is that referring to the *meta*-nitro compound, which, in view of an apparent failure of the Arrhenius equation, may not be significant. This relatively minor criticism is directed, not at minimizing the effect of induction, but at discovering what quantitative evidence may be adduced in its favour. It has, however, occasionally been misconstrued.<sup>†</sup> In its

† H. O. Jenkins, *ibid.*, 1780, (1939).

light we shall now examine the data of Table 14, to see how far the linear equation

$$E_s = E_u + K_1 \mu \quad (23)$$

alone can take us, without including the quadratic term representing the induction effect. Using the dipole moments of Sutton† and of McAlpine and Smyth,‡ we find, by the method of least squares, that

$$E_s = 18179 + 844.132\mu. \quad (24)$$

This linear equation gives the figures in the fourth column of Table 15. We note that the differences (last column) seldom exceed the difference between the experimental values found by the two teams of workers for a common reaction. We must also not overlook the possibility that a correction may be needed to allow for the variation of collision frequency with temperature, which, on account of the higher temperatures at which reactions with large energies are usually measured, will have a smoothing effect. All things considered, therefore, the experimental case has still to be made for the inclusion of the  $K_2 \mu^2$  term, and of still higher terms which in the ultimate analysis will doubtless be needed.

Table 15

*A Test of the Equation  $E_s = E_u + K_1 \mu$ , relating to the Reaction*



R	$\mu(\text{C}_6\text{H}_5\text{R}) \times 10^{18}$ e.s.u.	$E_A$ (calories/gram mole)		
		observed	calculated	difference
NH <sub>2</sub>	+ 1.55	20,000	19,487	+ 513
CH <sub>3</sub>	+ 0.45	18,200	18,559	- 359
H	0	17,700	18,179	- 479
F	- 1.57	17,200	16,854	+ 346
Cl	- 1.70	16,800	16,744	+ 56
NO <sub>2</sub>	- 4.19	14,650	14,642	+ 8

### *Elementary Formulation of the Energetics of Reactions between Ions and Molecules possessing two Dipoles*

Interesting and somewhat unexpected results are found when one traces the path followed by an ion under the influence of electrostatic fields simultaneously exerted from two points in one molecule.§ The problem has been only partially solved and, although exact

† *Loc. cit.*

‡ *J. Chem. Physics*, **3**, 55, (1935).

§ *Proc. Roy. Soc., A*, **157**, 667, (1936).

treatments lead to difficulties, much can be learnt, in a descriptive fashion, from elementary considerations.

There are good reasons for supposing that the energy of activation of such a reaction can be expressed in the form

$$E = E_0 + E_e(r_1) + E_e(r_2), \quad (25)$$

in which  $E_0$  embodies all the energy terms other than the two electrostatic ones. The first of these,  $E_e(r_1)$ , is a function of the critical distance,  $r_1$ , of the ion from the centre of the dipole which it is attacking; the second term,  $E_e(r_2)$ , is a function of the critical distance,  $r_2$ , between the ion at the point of attack and the centre of the second dipole, the role of which is that of an electrostatic witness rather than that of a direct chemical participant. Both  $E_e$  terms are functions also of Eulerian angles. In a series of reactions such as we have been considering,  $E_e(r_1)$  may be taken as having a constant value for each member, and may therefore be included with  $E_0$  as making up the energy of activation of the unsubstituted reaction. We then have directly (and dropping the subscript 2)

$$E_s = E_u + E_e(r). \quad (26)$$

Confining attention to infinite dilution, and assuming the field of the distant dipole to be exerted through a medium of uniform dielectric constant,  $D$ , we have

$$\frac{E_e}{N_0} = \frac{z\epsilon\mu \cos \theta}{Dr^2}, \quad (27)$$

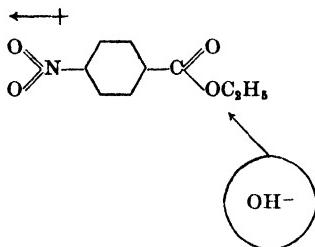
where  $z$  is the valency of the attacking ion,  $\mu$  is the dipole moment of the substituent group, and the other terms are as in equation (1).

Then

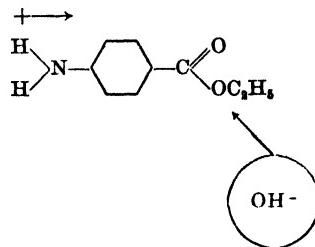
$$E_s = E_u + \frac{N_0 z \epsilon \mu \cos \theta}{Dr^2}. \quad (28)$$

If the dielectric constant does not vary with respect to temperature, this expression should be directly comparable with the experimental results. It implies, in the first place, that a common substituent dipole has an influence on the energy of activation which depends on the sign,  $z$ , of the attacking ion. This influence is illustrated in Fig. 7, in comparing the upper curve of which with Fig. 6, it should be noted that the ordinate scale is there inverted. When  $E_e$  is negative, electrostatic attraction aids the chemical reaction, and lowers the energy of activation. When  $E_e$  is positive, electrostatic repulsion makes things more difficult for the attacking ion, and the energy of activation is raised. We can thus readily understand why

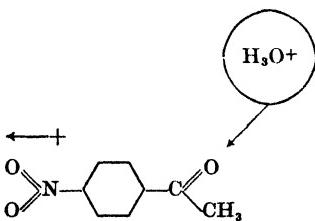
the substitution of a given group in a given position in the benzene ring affects the rates of acid-catalysed enolization and basic saponification in opposite ways:



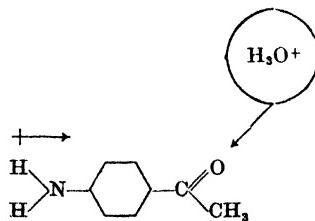
The field of the  $-\text{NO}_2$  dipole aids the approach of the attacking ion;  $E$  is thus lowered.



The field of the  $-\text{NH}_2$  dipole opposes the approach of the attacking ion;  $E$  is thus increased.



The field opposes ionic attack, and raises the energy of activation.



The field assists ionic attack, and lowers the energy of activation.

From equation (28) the empirical constant,  $K_1$ , of equation (21) receives the following quantitative interpretation:

$$K_1 = \frac{dE_s}{d\mu} = N_0 z\epsilon \cos \theta / Dr^2. \quad (29)$$

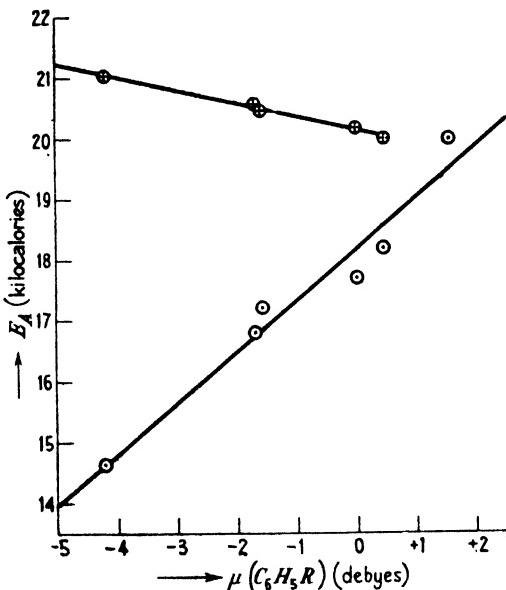
On the assumption that  $D$  is unity and temperature-invariant, we obtain, after inserting numerical values for the constants:

$$K_1 = \frac{dE_s \text{ (calories)}}{d\mu \text{ (debyes)}} = 69000 \frac{\cos \theta}{r^2 (\text{\AA})}. \quad (30)$$

Comparison with the experimental results obtained in the saponification of substituted ethyl benzoates (Table 14) leads to a value of  $82 \times 10^{-16}$  cm.<sup>2</sup> for  $r^2/\cos \theta$ . This result is an entirely reasonable one, and certainly correct as regards order of magnitude. (The same conclusion has also been reached by H. O. Jenkins† using the not very different method of plotting  $E_A$  against the electrostatic potential at

† Loc. cit.

zero ionic strength.) The distance across the benzene ring is 2.78 Å., and we can therefore work with an estimate of about 4.5 Å. as the distance,  $r$ , between the centre of the substituted dipole and the seat of chemical attack. On this supposition,  $\theta$  would be about 75°. If,



Upper curve:  $R.C_6H_4.COCH_3 + H_3O^+$ , giving a negative gradient.  
Lower curve:  $R.C_6H_4.COOC_2H_5 + HO^-$ , giving a positive gradient.

FIG. 7. The influence of *para*-substituents on reactions between ions and polar molecules.

on the other hand, we imagined the field effect to be transmitted through the solvent ( $D \doteq 25$  for ethyl alcohol), we would find that  $r^2/\cos\theta$  is about  $3.2 \times 10^{-16}$  cm.<sup>2</sup>, though a more careful analysis is here required as the true energy relationship then becomes

$$E_{A,s} = E_{A,u} - (LT-1) \frac{N_0 z \epsilon \mu \cos \theta}{Dr^2}, \quad (31)$$

which reduces to equation (28) only when  $L$  is zero. Though the balance of evidence is, on the whole, in favour of the former interpretation, the truth may well lie between the extremes represented by these tentative estimates.

An exact knowledge of  $D$  is neither available nor necessary for comparing the reactivities of, say, the *meta*- and *para*-derivatives

of otherwise identical molecules, for, from equation (29), we see that

$$\frac{K_m}{K_p} = \left(\frac{r_p}{r_m}\right)^2 \frac{\cos \theta_m}{\cos \theta_p}. \quad (32)$$

If the distances, rather than the angles, yield the dominant ratio, we would expect the slope  $dE_s/d\mu$  to be steeper for the *meta*-compound than for the *para*-compound, as seems to be the case in the enolization of the substituted acetophenones (Fig. 6). Now let us suppose that

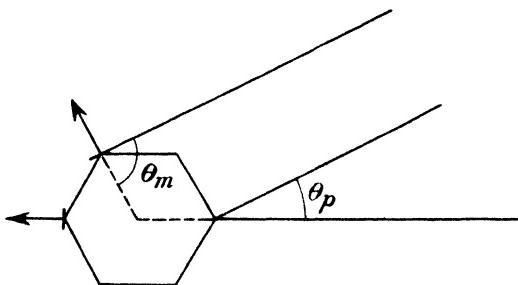


FIG. 8.

the common attacking ion approaches both molecules from the same direction, and in the plane of the benzene ring. We then have

$$\theta_m = \theta_p + \frac{1}{3}\pi, \quad (33)$$

as may be seen from Fig. 8. It follows that

$$\frac{K_m}{K_p} = \frac{1}{2} \left(\frac{r_p}{r_m}\right)^2 (1 - \sqrt{3} \tan \theta_p). \quad (34)$$

The experimental value of  $K_m/K_p$  may be as great as +2; any positive value requires that  $\theta_p$  is less than  $30^\circ$ . Similar expressions may readily be derived for substitution in the *ortho* position, and in the more general case where  $\theta$  is any angle of approach. In their light it becomes clear that simple electrostatics and the elements of geometry can dispel much of the perplexity from this ancient problem of the relative rates of substitution reactions.

### *Other Reactions between Ions and Polar Molecules*

Sets of reactions showing a constancy in  $A$  are not very numerous. The saponification of *para*-substituted ethyl benzoates offers an unusually suitable test for this constancy because, as Ingold has stressed, the point of ionic attack is separated from the electrostatic origin of the modifying field by the benzene structure. A similar

tendency is, however, apparent in the corresponding aliphatic reactions



Thus in passing from  $\text{R} = \text{CH}_3$  to  $\text{R} = \text{C}(\text{CH}_3)_3$ , the velocity is lowered 250-fold, whereas  $A$  is reduced only 5-fold (Table 16).† Comparable features are revealed by the hydrolysis of the same esters under the catalytic action of the hydrogen ion.‡ When changes in the reaction velocity are small, it becomes still more

Table 16

*The Saponification of Aliphatic Esters in 15 : 85 Aqueous-alcoholic Solution*

R	$k_{25^\circ\text{C.}} \times 10^3$	$A \times 10^{-6}$	$E_A$
CH <sub>3</sub>	6.21	1.60	14,200
C <sub>2</sub> H <sub>5</sub>	3.63	1.55	14,500
n-C <sub>3</sub> H <sub>7</sub>	1.72	1.72	15,000
n-C <sub>4</sub> H <sub>9</sub>	1.92	1.13	14,700
n-C <sub>5</sub> H <sub>11</sub>	2.07	1.47	14,800
n-C <sub>6</sub> H <sub>13</sub>	1.79	1.79	15,000
n-C <sub>7</sub> H <sub>15</sub>	1.84	1.84	15,000
iso-C <sub>3</sub> H <sub>7</sub>	0.80	0.54	14,500
iso-C <sub>4</sub> H <sub>9</sub>	0.43	1.38	15,700
(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )HC	0.33	6.40	15,400
(CH <sub>3</sub> ) <sub>3</sub> C	0.025	0.32	16,500
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> HC	0.016	0.90	17,400

difficult to decide whether  $E_A$  or  $A$  is responsible, or whether both vary, as they appear to in reactions of the type



where X = F, Cl, or Br and n = 1 or 2 (see Table 17).§ Earlier work (Table 1 of Chapter III) has proved that  $E_A$  increases as methyl iodide reacts, successively, with the *o*-, *m*-, and *p*-cresolate ions.

Values of  $P$  lying close to unity have been found for the bimolecular reactions between the hydroxyl ion and hexa-halogenoethanes in aqueous ethylalcoholic solution.||

The oxidation of certain aromatic compounds by the permanentanate ion in aqueous acidic solutions bears many of the marks of

† After D. P. Evans, Gordon, and Watson, *Trans. Chem. Soc.*, 1439, (1937).

‡ G. Davies and D. P. Evans, *ibid.*, 339, (1940).

§ After Bennett and B. Jones, *ibid.*, 1815, (1935); Baddeley and Bennett, *ibid.*, 1819, (1935).

|| W. Taylor and A. M. Ward, *ibid.*, 2003, (1934).

Table 17

Values of  $E_A$  (Kilocalories) for Reactions between Potassium Iodide and Substituted Benzyl Chlorides in 50 : 50 Acetone-Water Solution

Position:	<i>ortho</i>	<i>meta</i>	<i>para</i>
Substituent:			
F	17.2	18.4	17.8
Cl	16.9	17.7	18.0
Br	17.8	18.0	18.7
I	17.4	18.1	18.4
Average:	$17.3 \pm 0.5$	$18.0 \pm 0.4$	$18.2 \pm 0.5$

bimolecular reactions between ions and polar molecules, but the evidence is not conclusive,<sup>†</sup> particularly in view of the complex mechanism which oxidation reactions generally follow.<sup>‡</sup>

### The Variation in Kinetic Order of Reactions between Ions and Polar Molecules

In conformity with the hypothesis of activation outlined on p. 17, it is to be anticipated that any one of the reactions now considered may change from a bimolecular one to an apparently unimolecular one at relatively high concentrations, and that, if two reactions are examined at the same concentration, one may be of the second order while the other may be of the first order. The latter anticipation is the first to have been realized.

Slator<sup>§</sup> observed that alkyl halides and symmetrical ethylene di-halides react bimolecularly with sodium thiosulphate in water, but that the velocity of reaction with iodochlorethane and bromochlorethane was independent of the concentration of thiosulphate. A transition in kinetic order may thus result from a very slight modification in the structure of one of the reactants. E. D. Hughes and Ingold have shown that (1)  $\beta$ -phenylethyltrimethylammonium hydroxide decomposes bimolecularly, whereas halides of the corresponding *p*-nitro derivative decompose unimolecularly, and that (2) the velocity of hydrolysis of both ethyl chloride and tertiary butyl chloride depends on their concentration, but only in the former case is it influenced by the concentration of alkali, and (3) the elimination

<sup>†</sup> Hinshelwood, *Trans. Chem. Soc.*, 1180, (1919); Moelwyn-Hughes and Musgrave, *Trans. Faraday Soc.*, 29, 1162, (1933); Hinshelwood and Winkler, *Trans. Chem. Soc.*, 368, (1936).

<sup>‡</sup> See, for example, J. Bradley and van Praagh, *ibid.*, 1624, (1938).

<sup>§</sup> *Loc. cit.*

of methyl alcohol and tertiary butyl alcohol from substituted sulphonium hydroxides are processes of the second and first order respectively. These interesting observations they have turned to good account by using the change of kinetic order as part of a general diagnosis of mechanism in organic reactions. (See references on p. 137).

The transition in order has also been discussed† in terms of the average lifetime,  $t$ , of the organic reactant. The time elapsing between two successive collisions is, from equation (19) of Chapter I, found to be

$$t = \frac{1}{n(r_A + r_B)^2} \left( \frac{\mu}{8\pi kT} \right)^{\frac{1}{2}}. \quad (35)$$

On substituting numerical values for the constants, and converting the concentration unit from  $n$  molecules/c.c. to  $c$  gram molecules/litre, we have the approximate relationship

$$t = \frac{3.5 \times 10^{-12}}{c} \text{ second.} \quad (36)$$

Taking  $c$ , from Slator's work, to have the order of magnitude  $10^{-2}$ , we estimate the average lifetime of one of the activated reactants as  $3.5 \times 10^{-10}$  second. The interest lies less in the numerical result, though it is not an unreasonable one, than in the evidence afforded that molecules are not activated solely by collisions which lead to chemical reaction, but can receive their energy of activation in previous collisions.‡

### *The Influence of the Solvent*

Relatively little work has been done on varying the solvent environment. Tsu-Chung Huang and Ho-Sheng Hsieh§ have established a linear relationship between the bimolecular velocity coefficient,  $k_D$ , governing the saponification of methyl acetate at 25° C., and the molar fraction  $N_D$ , of dioxan in the aqueous solution:

$$k_D/k = 1 + 5.85N_D. \quad (37)$$

The chief effect of displacing water by the organic solvent is most probably accounted for by its influence in lowering the dielectric

† *Nature*, January 1934.

‡ Cf. Read and W. Taylor (*Trans. Chem. Soc.*, 478, (1939)), who find that triphenyl-chlormethane and water react bimolecularly in dioxan solution.

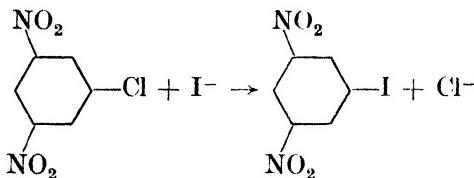
§ *J. Chinese Chem. Soc.*, 7, 1, (1939).

constant, which, according to equation (11), can be represented as follows:

$$\frac{d \ln k^0}{d(1/D)_T} = -\frac{z_A \epsilon \mu_B \cos \theta}{r^2 k T}. \quad (38)$$

Recalling that  $z_A \epsilon \mu \cos \theta$  has a negative sign, we see that the observed effect is in agreement with this equation. The experiments, however, do not extend to molar fractions beyond  $\frac{1}{10}$ . When much more dioxan is present, we may anticipate a rather severe falling-off in the rate, comparable to that found in the racemization of 2-methylbutanal-1, catalysed by hydrogen ion.<sup>†</sup> In spite of the conventional way in which the saponification of esters is written, the smooth reaction almost certainly requires the presence of more than one molecule of water for each molecule of ester. The continuous replacement of water by chemically inert media may thus well accelerate the rate of reaction for small additions, until a point is reached—possibly quite suddenly—when the reaction is stifled for lack of water.

The reaction



has been studied in ethylene glycol solution by Bennett and (Miss) Vernon,<sup>‡</sup> from whose data the bimolecular velocity constant may be expressed as follows:  $k \doteq 3.5 \times 10^{10} e^{-28000/RT}$ .

Compared with other reactions in the class under discussion, the absolute rate of the present one is slow, and it is therefore noteworthy that satisfactory agreement with the simple collision formula is still maintained. The only complication present would appear to be the reverse reaction, for which the authors have made allowance.

#### *Reactions between Ions and Non-polar Molecules*

The principal electrostatic energy to be considered in reactions between ions and non-polar molecules is the term (cf. equations (14) and (15) of Chapter III):

$$\frac{E_e}{N_0} = -\frac{1}{2} \alpha F^2 = -\frac{1}{2} \frac{\alpha z^2 \epsilon^2}{D^2 r^4}, \quad (39)$$

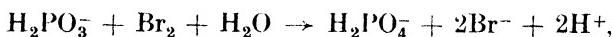
<sup>†</sup> Badin and Paesu, *J. Amer. Chem. Soc.*, **67**, 1352, (1945).

<sup>‡</sup> *Trans. Chem. Soc.*, 1783, (1938).

which represents the net energy of interaction between the ion and the dipole which its field induces in the molecule. There are insufficient data to allow of a decision as to how far this energy affects the kinetics of reactions in solution. Indirect computations (see p. 164) of the bimolecular velocity coefficient of the reaction between the iodide ion and the iodine molecule in aqueous solution



leads to a value of  $k_2 \doteq 4 \times 10^{11}$  litres/gram mole-second, which is quite a likely figure, having regard to the uncertainties in the equilibrium data. The kinetics of the bimolecular reaction



also in aqueous solution, has been studied by Griffith and McKeown, whose results† may be summarized in the form

$$k_2 = 6.0 \times 10^{10} \times e^{-15100/RT}$$

Here again there are indications of normal behaviour. On the other hand, the absolute rate of the reaction



is a high one, which, if we compare it with the equation

$$k_2 = Ze^{-E/RT}e^{+2\alpha^2\epsilon^2/D^2r^4kT}, \quad (40)$$

leads to values of  $r$  ranging from  $(0.6 \text{ to } 6.0) \times 10^{-8}$  cm., according to the dielectric constants (80 to 1) employed.

### *The Energy of Activation of Reactions between Ions and Polar Molecules*

If only the direct field and the induction effects are taken into account, the total energy of interaction of an ion and a dipole consists of the two familiar terms

$$\frac{E_c}{N_0} = \frac{z_B \epsilon \mu_A \cos \theta}{Dr^2} - \frac{\alpha(z_B \epsilon)^2}{2(Dr^2)}, \quad (41)$$

the first of which may denote a repulsion or an attraction, according to the value of the angle,  $\theta$ . The conditions for a minimum energy are that  $dE_c/d\theta$  and  $dE_c/dr$  shall both be zero. The first condition simply gives us  $\theta = 0$ , reminding us again of the most favourable inclination for attraction. The second condition yields a minimum value of  $r$  equal to  $(z_B \epsilon \alpha / D \mu_A)^{1/2}$ , which is an imaginary distance in

† *Trans. Faraday Soc.*, **29**, 611, (1933).

the cases of interest ( $z_B$  is negative). Other energy terms must be lacking. The most probable one is the strong repulsion which manifests itself when the ion and dipole get close together. If we assume the force of repulsion to vary exponentially with the separation, as Born and Mayer (*vide infra*) have done, the energy of interaction of a univalent negative ion with a dipole placed in the attractive position along the extended polar axis, and at a distance  $r$  from its centre is

$$u = V e^{-br} - \frac{\epsilon \mu}{r^2} - \frac{\alpha \epsilon^2}{2r^4}. \quad (42)$$

Here  $V$  and  $b$  are specific constants, and  $D$  is taken to be unity for the close approach considered. Arguing along these lines, Ogg and Polanyi† have made the first successful attempt at computing, without reference to kinetic data, the energy of activation of a reaction in solution. The governing principle (Heitler and London, p. 14) is that an energy barrier must be surmounted before the initial system  $AB\dots C$  can be converted into the final system  $A\dots BC$  and that the lowest height of the barrier consonant with minimum differences in the interatomic distances may be identified with the energy of activation. Its application to reactions in solution necessitates the introduction of additional, and rather important, terms to take account of the solvation energies, and may be illustrated by considering in detail Ogg and Polanyi's method of obtaining the energy of activation of the reaction



in acetone solution.

It is postulated that the hydrogen atoms in the critical complex are co-planar, and that the energy required to fan them out into this position may be neglected—a postulate for which there is some quantal support.‡ The mechanism of reaction, consistent with the optical inversion, can then be represented as in Fig. 9.

It can be seen that the halide molecule, during reaction, is turned inside out, like an umbrella in a strong wind. The initial system, to which a potential energy of zero may arbitrarily be assigned, corresponds to a solvated iodine ion at an infinite distance away from the molecule  $\text{CH}_3\text{Cl}$ , the groups of which are at the equilibrium separation  $r_0$ . The activation energy is the minimum energy which the

† *Trans. Faraday Soc.*, 31, 604, (1935).

‡ Penney, *ibid.*, p. 734, (1935).

system must acquire before reaction can occur; in other words, it is the height of the pass in the three-dimensional energy model. The negative charge on the ion and the nature of the dipole moment of

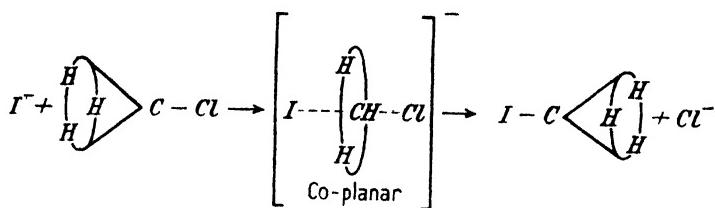


FIG. 9.

the molecule predispose the line of attack to be along the axis of the C—Cl bond. Omitting the hydrogen atoms, we then have the scheme of things illustrated in Fig. 10.

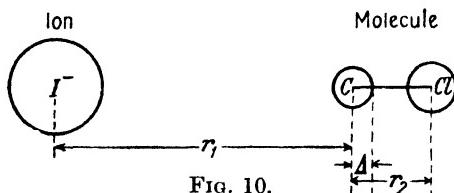


FIG. 10.

In order to bring the system from its initial position up to the stage shown in the diagram, we must, according to equation (6) of Chapter III, expend an energy

$$D_{\text{CH}_3\text{Cl}} \{ 1 + e^{-2a(r_2 - r_0)} - 2e^{-a(r_2 - r_0)} \}$$

to distend the molecule from the separation  $r_0$  to  $r_2$ . We must also expend an energy  $-\frac{\epsilon \mu_{\text{CH}_3\text{Cl}}}{(r_1 + \Delta)^2} - \frac{\alpha e^2}{2r_1^4} + V(I)e^{-br_1}$  in bringing the ion  $\text{I}^-$  from infinity up to the distance  $r_1$ . This approach is aided by the interaction between the ion and the dipole, and by the polarizability of the carbon atom (hence the negative sign of these two terms), and is resisted by the interpenetration of the fields of the iodide ion and the completely substituted carbon atom.  $\mu_{\text{CH}_3\text{Cl}}$  is the dipole moment of the molecule  $\text{CH}_3\text{Cl}$ .  $\alpha$ , the polarizability of the carbon atom, is obtained from bond refractivities.  $\Delta$  is the 'radius' of the carbon atom, at the rim of which the dipole is taken to be situated.  $V$  and  $b$  are constants of the repulsive field between the iodine atom and the fully loaded carbon atom, and are slightly modified values of the

figures for crystals.<sup>†</sup> To these four terms we add the energy  $S_{I^-}$  which is the work which must be performed on the system to liberate the iodine ion from its union with a single molecule of solvent. We therefore have for the total potential energy of the system:

$$E_1 = S_{I^-} + D_{\text{CH}_3\text{Cl}} \{1 + e^{-2a(r_1 - r_0)} - 2e^{-a(r_1 - r_0)}\} - \frac{\epsilon\mu_{\text{CH}_3\text{Cl}}}{(r_1 + \Delta)^2} - \frac{\alpha\epsilon^2}{2r_1^4} + V(\text{I}^-)e^{-br_1}. \quad (43)$$

Here,  $a$  and  $r_0$  refer to  $\text{CH}_3\text{Cl}$ , and  $V$  and  $b$  refer to  $\text{I}^-$ .

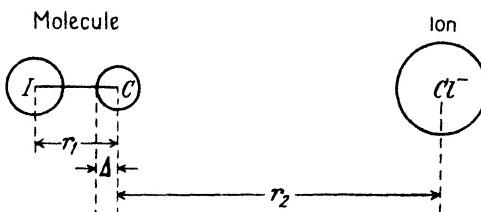


FIG. 11.

Similarly, if we consider the complex to be formed from the opposite direction, we have the configuration shown in Fig. 11, for which the energy is

$$E_2 = S_{\text{Cl}^-} + D_{\text{CH}_3\text{I}} \{1 + e^{-2a(r_1 - r_0)} - 2e^{-a(r_1 - r_0)}\} - \frac{\epsilon\mu_{\text{CH}_3\text{I}}}{(r_2 + \Delta)^2} - \frac{\alpha\epsilon^2}{r_2^4} + V(\text{Cl}^-)e^{-br_2}. \quad (44)$$

Now,  $a$  and  $r_0$  refer to  $\text{CH}_3\text{I}$ , and  $V$  and  $b$  to  $\text{Cl}^-$ .

The problem is to determine values of  $r_1$ ,  $r_2$ ,  $E_1$ , and  $E_2$  such that  $r_1$  and  $r_2$  may simultaneously and independently have the same values in the two equations, while  $E_1$  and  $E_2$  are both equal and minimal. The solution is found graphically, in the following manner. Selecting an arbitrary value of  $r_1$ , we represent  $E_1$  as a Morse function of  $r_2$ , displaced vertically by an amount dependent on the constant value of  $r_1$  chosen. Similarly, still with the same fixed value of  $r_1$ , we express  $E_2$  as a Born-Mayer function in  $r_2$ , displaced vertically by an amount dependent on the value of  $r_1$  chosen. The type of curve found is shown in Fig. 12, where  $r_1$  was kept at a constant value of  $2.80 \text{ \AA}$ . The point of intersection of the two curves gives a 'pass height' of  $2.29 \times 10^{-12}$  ergs per molecule. Proceeding with a new value of  $r_1$ , we construct another pair of curves, and find another value for the energy corresponding to the intersection; the minimum

<sup>†</sup> Born and J. E. Mayer, *Z. für Physik*, **75**, 1, (1932).

value of this quantity is the energy of activation, on the basis of the various postulates underlying the treatment. A careful examination of the curves in Fig. 12 shows that they are of similar forms; the flatter of the two has also a minimum, and appears very similar to the other

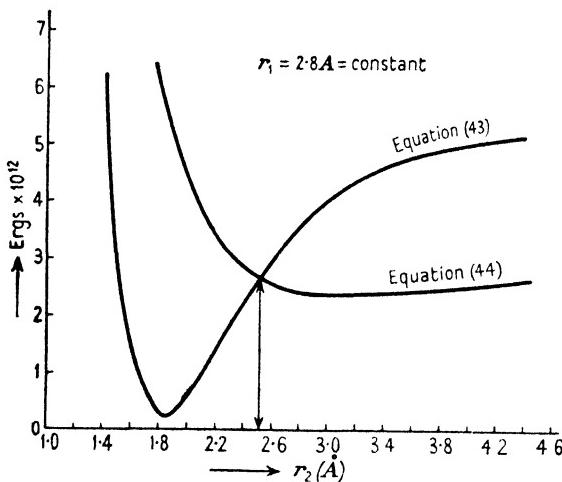


FIG. 12.

curve when plotted on a suitable scale. At the relevant distances and energies the net interaction of the ion and the dipole is one of repulsion.

The energy of interaction of the iodide ion and the acetone molecule may be expressed in the form

$$S_{I^-} = V(I^-)e^{-br_s} - \frac{\epsilon\mu_s}{(r_s + \Delta)^2} - \frac{\alpha\epsilon^2}{2r_s^4} \quad (45)$$

in which  $\mu_s$  is now the dipole moment of the solvent molecule, and the separation,  $r_s$ , refers to the solvate. The minimum value of  $S_{I^-}$  is the energy of solvation. For the iodide ion it is found to be  $-10.6$  kilocalories and for the chloride ion  $-13.2$ ; both results are in reasonable agreement with indirect estimates based on the lattice energy of the crystalline salts and the heats of dissolution.

The results calculated by Ogg and Polanyi† are shown in Table 18, along with those obtained in a repetition of their calculations.‡ Experimental values are not available. The apparent energy of activation for the reactions of a series of alkyl halides with potassium

† *Loc. cit.*‡ *Acta Physicochim. U.S.S.R.*, **4**, 173, (1936).

Table 18

*The Determination of Critical Interatomic Distances and the Energy of Activation of the Reaction  $\text{CH}_3\text{Cl} + \text{I}^- \rightarrow \text{CH}_3\text{I} + \text{Cl}^-$*

	$r_1(\text{I}^- - \text{CH}_3\text{Cl}) \times 10^8 \text{ cm.}$	$r_2(\text{Cl} - \text{C}) \times 10^8 \text{ cm.}$	$E$ (kilocal.)
Original	2.56	2.18	28.5
Repetition	2.54	2.18	28.9

iodide in acetone solution is 18.9 (Table 4), which is subject to a correction of about 2.1 kilocalories before the computed values, which refer to a system at constant volume, can be compared with the experimental value which refers to a constant pressure (p. 355). Acetone is a notoriously difficult solvent to obtain dry, and the presence of water usually acts as a catalyst, reducing the value of  $E_A$  by probably 1–2 kilocalories. The experimental value for the reaction considered is thus probably no less than 22 kilocalories per gram mole. All things considered, the agreement with the calculated value is satisfactory.

According to these estimates,  $E$  should have nearly the same value for the replacement by the iodine atom of the chlorine atom in other alkyl chlorides. In Table 19, the second column gives the bimolecular velocity coefficients for four racemizations,† and the last column the values of the apparent energies of activation which experience teaches us may be associated with reactions having these velocities in this solvent. There can be no doubt about the agreement, in a general way, between such experimental values and those estimated theoretically.

Table 19

*The Velocity of Certain Racemizations in Acetone Solution*

Reaction	$k_{50^\circ\text{C}}$ (observed)	$E_A$ (estimated experimentally)
Methylbutylfluoromethane + $\text{F}^-$	$2.2 \times 10^{-8}$	27.5–29.7
" + $\text{Cl}^-$	$2.0 \times 10^{-7}$	24.0–26.8
" + $\text{Br}^-$	$1.2 \times 10^{-4}$	20.5–22.7
" + $\text{I}^-$	$2.3 \times 10^{-3}$	18.5–20.9

There are few deficiencies in the theory of which its authors are not themselves aware. The possibility of the simultaneous existence of two critical complexes  $\text{I}^- \dots \text{C} \dots \text{Cl}$  and  $\text{I} \dots \text{C} \dots \text{Cl}^-$  with the same

† Bergmann, Polanyi, and Szabo, *Trans. Faraday Soc.*, **32**, 843, (1936).

energy necessitates some correction for the resonance which may exist between them. According to the quantum theory, the effect of resonance in this case is to lower the energy of activation, but the omission of the correction is to some extent balanced by the omission of the forces exerted between the attacking ion and the three hydrogen atoms. Secondly, the difference between the value of  $r_2$  (2.18 Å.) for the critical complex and the equilibrium separation,  $r_0$  (1.85 Å.), between the carbon and chlorine atoms, indicates that the active molecule must be in a state of violent oscillation, with a vibrational energy of 14.5 kilocalories, corresponding to seven quanta,  $\hbar\nu_0$ , of vibrational energy. There is left some 14.0 kilocalories which may be entirely kinetic energy. The mechanism is therefore too limited in that it does not allow a sufficiently elastic distribution of energy. Thus, for example, in the present case, the acquisition of 20.0 kilocalories as vibrational energy and 8.5 as kinetic energy would not produce chemical reaction, though the sum is sufficient. The necessary averaging process, however, cannot be carried out until we know much more than we do at present about the conditions governing the conversion of translational energy to vibrational energy.

## VI

## EQUILIBRIA

CHEMICAL changes, like all good things, come to an end. The kinetic description of the kind of end reached, first given by Berthollet and by Pean de St. Giles,<sup>†</sup> is a state of balanced activity rather than one of rest. Molecules are then formed at the same rate as they are destroyed, and no chemical change is discernible. How long it takes a chemical reaction to come to an end depends on a number of specific factors; theoretically, it takes an infinity; experimentally, any reaction can be regarded as over in a time which is about 100 times as great as that required for the reaction to go half-way. We have now to see what form is assumed by some of the kinetic laws derived in Chapter II when they are applied to systems allowed to react for very long periods of time.

Let us first consider the reversible reaction represented by the equation



Here  $k_1$  and  $k_2$  are unimolecular constants, and  $a$  and  $b$  the initial concentrations of reactant and resultant, respectively. The fractional change after a time  $t$  is:<sup>‡</sup>

$$\frac{x}{a} = \frac{k_1 - k_2(b/a)}{k_1 + k_2} [1 - e^{-(k_1 + k_2)t}] \quad (2)$$

When  $t$  is infinite, this equation reduces to

$$\left( \frac{b+x}{a-x} \right)_{t=\infty} = \frac{k_1}{k_2}. \quad (3)$$

But  $(a-x)_\infty$  and  $(b+x)_\infty$  are the time-invariant concentrations of the two molecular species present at the completion of the reaction. Denoting the end concentration by  $c$ , we thus find that

$$\frac{c_B}{c_A} = \frac{k_1}{k_2} = K. \quad (4)$$

The time-invariant ratio of the product of the concentrations of the

<sup>†</sup> See A. J. Berry, *Modern Chemistry*, Cambridge, (1946).

<sup>‡</sup> Lowry, *Trans. Chem. Soc.*, 75, 212, (1899); cf. equation II (7).

resultant molecular species to the product of the concentrations of the reactant molecular species in any system is known as the equilibrium constant, and is usually denoted by the letter  $K$ .

A reactant,  $A$ , decomposing unimolecularly, may be reformed bimolecularly according to the scheme:



The fractional change after a lapse of time,  $t$ , is then

$$\frac{x}{a} = \left[ \frac{1}{2} + \frac{k_2}{k_1} \alpha \coth(k_2 \alpha t) \right]^{-1}, \quad (6)$$

where

$$\alpha^2 = \frac{k_1}{k_2} a + \left( \frac{k_1}{2k_2} \right)^2. \quad (7)$$

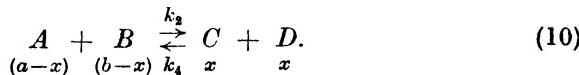
As  $t$  becomes infinite, this expression reduces to

$$\left( \frac{x^2}{a-x} \right)_{t=\infty} = \frac{k_1}{k_2}, \quad (8)$$

or, again denoting the final concentration by  $c$ , we obtain

$$\frac{c_B c_C}{c_A} = \frac{k_1}{k_2} = K. \quad (9)$$

Finally, let us examine the kinetic laws which govern reversible bimolecular changes, such as:



The appropriate kinetic law in such cases is (cf. equation II (9)):

$$x = \frac{ab}{1-K} \{ \alpha + \beta \coth[\beta(k_2 - k_4)t] \}^{-1}. \quad (11)$$

Here,

$$K = k_4/k_2, \quad (12)$$

$$\alpha = (a+b)/2(1-K), \quad (13)$$

and

$$\beta = [(a-b)^2 + 4Kab]^{1/2}/2(1-K). \quad (14)$$

Again, when  $t$  becomes infinite, we see that the kinetic law for the final state of the system is

$$\frac{c_C c_D}{c_A c_B} = \frac{k_2}{k_4} = K. \quad (15)$$

Quite generally, when the rate of an advancing reaction can be expressed by the kinetic law

$$+\frac{dc}{dt} = k_1 c_A^{m_1} c_B^{m_2} c_C^{m_3} \dots, \quad (16)$$

and the rate of the opposing reaction can be represented by the kinetic law

$$-\frac{dc}{dt} = k_2 c_L^{n_1} c_M^{n_2} c_N^{n_3} \dots, \quad (17)$$

the conditions that there shall be no variation of chemical composition with respect to time are

$$K = \frac{c_L^{n_1} c_M^{n_2} c_N^{n_3} \dots}{c_A^{m_1} c_B^{m_2} c_C^{m_3} \dots}, \quad (18)$$

and

$$K = \frac{k_1}{k_2}. \quad (19)$$

The elimination of time from kinetic expressions thus leads to the law of mass-action, and to other simplified expressions which may be treated by the methods of thermodynamics.

Chemical kinetics regards all systems as changing, and looks upon the equilibrium state of matter as a special one, in which change continues but is undetectable. Thermodynamics, on the other hand, deals exclusively with systems showing no temporal change; reacting systems are outside its province.

The free energy,  $A$ , of a system of  $N$  molecules in a gas which obeys the ideal laws at a temperature  $T$  is well known to be related as follows to the concentration  $c$ :

$$A = A^0 + NkT \ln c. \quad (20)$$

Whether we express  $c$  in the units of gram moles per litre, or molecules per c.c., or in any other unit, the meaning of  $A^0$  is clearly the free energy of the  $N$  molecules when their concentration is unity. The free energy of real gases and of solutes can seldom be represented by such a simple equation, and for that reason, a corrected concentration, termed the activity, is introduced to make things fit.† Then

$$A = A^0 + NkT \ln a. \quad (21)$$

In terms of the various activities, the law of mass-action assumes the form

$$K = \frac{a_L^{n_1} a_M^{n_2} \dots}{a_A^{m_1} a_B^{m_2} \dots}. \quad (22)$$

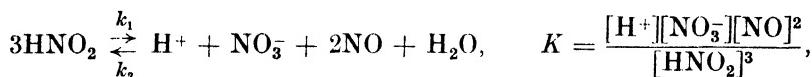
† G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Co., New York, (1923).

In this form, equilibria in solution can be represented, whether they be decompositions, polymerizations, or ionizations. The expression is, by definition, applicable to equilibrium systems in various media, and, in the form of the distribution laws, to heterogeneous systems.

*The Velocities of Reaction at the Equilibrium Stage; Verification of the Law  $K = k_1/k_2$*

The equivalence of the static and dynamic definitions of chemical equilibrium has been verified in a number of instances, of which two may be cited.

From static measurements, the equilibrium constant for the system

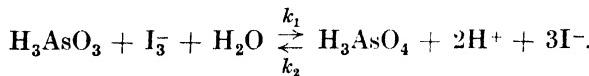


has been found to diminish with an increase in dilution, reaching a limiting value of about 30† in aqueous solution at 25° C. The kinetic expressions for the direct and reverse reactions are

$$\begin{aligned} -\frac{d[\text{HNO}_2]}{dt} &= k_1[\text{HNO}_2]^4/[\text{NO}]^2, \\ +\frac{d[\text{HNO}_2]}{dt} &= k_2[\text{HNO}_2][\text{H}^+][\text{NO}_3^-]. \end{aligned}$$

The ratio ( $k_1/k_2$ ) of the two velocity constants similarly changes with the dilution, the extrapolated value being about 35.‡

Our second example is afforded by the work of Roebuck,§ Bray,|| and Liebhafsky†† on the following equilibrium:



At 0° C.,  $k_1/k_2 = 0.15$ , and  $K = 0.16$ . The agreement in both cases is as close as the omission of any correction for salt effects will allow.

Apparent exceptions to the validity of equation (19) may be traced

† Abel and Schmid (*Z. physikal. Chem.*, **132**, 56, (1928); **134**, 279, (1928); **136**, 430, (1928)) give 29, while G. N. Lewis and M. Randall (*Thermodynamics*, p. 564, (1923)) give 31.

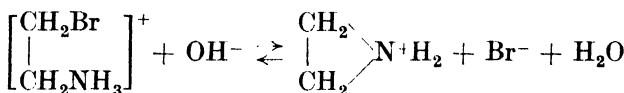
‡ Abel, Schmid, and Babab, *Z. physikal. Chem.*, **136**, 135, 419, (1928); Abel, Redlich, and Lengyel, *ibid.*, **132**, 189, (1928).

§ *J. Physical Chem.*, **6**, 365, (1902).

|| *Ibid.*, **9**, 578, (1905).

†† *Ibid.*, **35**, 1648, (1931).

to inaccurate applications or to false equilibrium conditions. For example, the static analysis of the system



gave an 'equilibrium constant' which could not be reproduced by heating the system and reverting to the original temperature. The disparity between dynamic and static measurements previously believed to exist† is thus not real.‡

### *The Indirect Determination of Velocity Coefficients*

Equation (19) is often found convenient for determining, by indirect means, the velocity of a reaction which is too slow or too fast to be measured directly. It is also helpful in ascribing a velocity coefficient to a reaction when the equilibrium position lies far over to one side, and when the analytical range is therefore limited.

The equilibrium constant  $K$  for the system



in benzyl alcohol solution at 80° C. is  $K = [AB]/[A][B] = 1.64$  litres per gram molecule.§ The unimolecular velocity constant  $k_1$  for the decomposition of triethylsulphonium bromide Corran finds to be  $1.48 \times 10^{-5}$  seconds<sup>-1</sup>, in good agreement with von Halban's value of  $1.50 \times 10^{-5}$ .|| It follows that the bimolecular constant  $k_2$  for the combination reaction is  $2.44 \times 10^{-5}$  litres/gram molecule-second.††

From the ionic product of water at 25° C. we can say that the ions recombine about  $4 \times 10^{15}$  times as fast as the water molecules dissociate, although the absolute speed of either change is not known. Statistical equilibrium is maintained between a small number of hydrogen and hydroxyl ions combining rapidly and a large number of water molecules dissociating slowly. If we ascribe an average lifetime of about  $10^{-13}$  seconds to the activated water molecules, we see that the rate of combination of the ions is extremely rapid. In fact, it would appear that the only condition for the union of the two ions is that they meet each other.‡‡

† Freundlich and Neumann, *Z. physikal. Chem.*, **87**, 69, (1914).

‡ Freundlich and Kroepelin, *ibid.*, **122**, 39, (1926).

§ Corran, *Trans. Faraday Soc.*, **23**, 605, (1927).

|| *Z. physikal. Chem.*, **67**, 129, (1909).

†† I have here corrected an error which appeared in my previous calculations (*Chemical Reviews*, **10**, 241, (1932)).

‡‡ *The Kinetics of Reactions in Solution*, 1st ed., p. 123, (1933).

One instance confirming this view may be quoted. The electrical conductivity of an ethylalcoholic solution of ammonia rises slowly during storage, possibly due to a slow dissociation of the ethyl alcohol into ethoxide and hydrogen ions, which then react rapidly with the solute.<sup>†</sup> If this is the correct explanation, the velocity coefficient of the ionization process, regarded as a unimolecular one, is about  $3 \times 10^{-8}$  sec.<sup>-1</sup> The ionic product of alcohol at the same temperature (25° C.) is known to be  $1.9 \times 10^{-19}$  (gram-ions/litre)<sup>2</sup> (see p. 236). Hence  $k_2$  is about  $1.5 \times 10^{11}$  litres/gram mole-second, which is the figure one would expect for the velocity of a bimolecular reaction requiring no energy of activation.<sup>‡</sup>

### *The Relation between the Heat of Reaction and the Energies of Activation*

By combining the van 't Hoff isochore,

$$\left( \frac{d \ln K}{dT} \right)_P = \frac{\Delta H}{RT^2}, \quad (23)$$

and the Arrhenius equation,

$$\left( \frac{d \ln k}{dT} \right)_P = \frac{E_A}{RT^2}, \quad (24)$$

with equation (19), we see that

$$\Delta H = E_1 - E_2. \quad (25)$$

The heat absorbed during a chemical reaction is, therefore, equal to the difference between the energies of activation of the direct and reverse processes.

This equation has received inadequate verification. Most of the examples in the literature which show an excellent concordance between  $\Delta H$  and  $(E_1 - E_2)$  are algebraic necessities following the inclusion of the equilibrium constant,  $K$ , in the kinetic expressions for  $k_1$  and  $k_2$ , from which  $E_1$  and  $E_2$  are subsequently evaluated. This is the case, for example, in the extensive data on the kinetics of the interaction of diols and acetone in the presence of water.<sup>§</sup> When, however, the calorimetric value of  $\Delta H$  and the kinetic value of  $(E_1 - E_2)$  are both available, it is found that equation (25) is obeyed

<sup>†</sup> Ogston, *Trans. Chem. Soc.*, 1023, (1936).

<sup>‡</sup> Ogston gives a bimolecular dissociation constant, but the argument and the numerical answer are independent of the order assumed for the ionization.

<sup>§</sup> Hermans, *Z. physikal. Chem.*, 113, 337, (1924).

within the limits of experimental error. The interconversion of urea and ammonium cyanate in water is the best known instance, for which we have:

$(\text{NH}_2)_2\text{CO} \rightarrow \text{NH}_4^+ + \text{CNO}^-$	$E_1 = 31,300\ddagger$
$\text{NH}_4^+ + \text{CNO}^- \rightarrow (\text{NH}_2)_2\text{CO}$	$E_2 = 23,200\ddagger$
$\Delta H$ (kinetic) = $E_1 - E_2$	8,100
$\Delta H$ (calorimetric)	7,400§
$\Delta H$ (from equation (23))	7,600

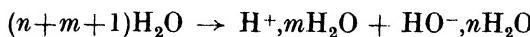
When the opposing reactions set up a highly symmetrical equilibrium, as is the case in many optical inversions, the difference between the two energies of activation may be so small as to be hardly detectable by the most accurate kinetic measurements.†† Some examples of mutarotations in aqueous solution are recorded in Table 1.††

Table 1

*Kinetic Determination of the Heat Effect attending the Mutarotation of Certain Sugars in Water at 298.1° K.*

Reaction	$E_1$	$E_2$	$\Delta H$
$\alpha$ -Xylose $\rightarrow$ $\beta$ -xylose	16,245	16,795	-550
$\alpha$ -Mannose $\rightarrow$ $\beta$ -mannose	16,375	16,375	0
$\alpha$ -Glucose $\rightarrow$ $\beta$ -glucose	16,945	16,945	0
" "	(16,858)	(17,033)	-175
$\alpha$ -Lactose $\rightarrow$ $\beta$ -lactose	17,225	16,515	+710

When the energy of activation of one of the reactions is zero the energy of activation of the other reaction equals the heat absorbed. Regarding the union of the hydrogen and hydroxyl ions in water as requiring no critical energy, we infer that the value of  $E_1$  for the ionization



at 298.1° K. must be 13,650 calories.

† Burrows and Fawcett, *Trans. Chem. Soc.*, **105**, 609, (1914).

‡ Walker and Hambly, *ibid.*, **67**, 746, (1895).

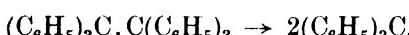
§ Walker, *Z. physikal. Chem.*, **42**, 207, (1902).

|| Lineken and Burrows, *J. Amer. Chem. Soc.*, **51**, 1106, (1929).

†† See also Sturtevant (*ibid.*, **59**, 1528, (1937)). Rowe and Parks (*J. Chem. Physics*, **14**, 383, (1946)) find  $\Delta H$  for the mutarotation of  $\alpha$ -glucose to be  $-175 \pm 5$  calories per gram mole, by calorimetry. The bracketed values of the energies of activation are based on this figure.

‡‡ Moelwyn-Hughes and Kendrew, *Proc. Roy. Soc., A*, **176**, 352, (1940).

The chief uses of equation (25) up to the present time have been in assessing one of the three terms from a knowledge of the other two. The unimolecular constant for the dissociation of hexaphenylethane, for example,



in chloroform solution and in numerous other solvents, is

$$k_1 = (3.6 \pm 2.6) \times 10^{12} \times e^{-(19100 \pm 1400)/RT}.$$

From the rate of combination of the free radicals in the same media the value of  $E_2$  is found to be 3,600 calories.† The increase in heat content attending dissociation in solution is thus about 15,500 calories, and the value in the gaseous phase, which will probably be some 5,000 calories greater (p. 180), is still of a lower order of magnitude than the energy required to break the link joining the two carbon atoms in any unsubstituted paraffin.

### *Chemical Equilibria in the Gaseous Phase*

At a given temperature and pressure, the equilibrium constant,  $K$ , may be expressed by either of the equivalent relations,

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (26)$$

and

$$K = We^{-\Delta H^0/RT}, \quad (27)$$

in which  $\Delta S^0$  ( $= R \ln W$ ) is the difference between the molar entropy of the products and the molar entropy of the reactants in a reference state (p. 328). Generally, both  $\Delta S^0$  and  $\Delta H^0$  are functions of the temperature, but for simple gaseous equilibria the variation is often too small to be detected by measuring the change of  $K$  with respect to  $T$ . On plotting  $\ln K$  against  $1/T$  for such systems, we find the results shown in Table 2. The state of reference is the gaseous state at a concentration of 1 gram mole per litre.

The quantity  $\Delta S^0$  can thus be found directly from experiments on the equilibrated systems at various temperatures. It can also be found by measuring calorimetrically the separate entropies of reactants and resultants in the standard states to which  $K$  refers, and by accepting the molar entropy of all pure crystals at the absolute zero of temperature as being itself zero. This is the content of the third law of thermodynamics, a discussion of which would take us far afield. When the molecules taking part in the chemical reaction

† Ziegler, Fr. Ewald, and Orth, *Annalen*, **479**, 277, (1930); Ziegler, Orth, and Weber, *ibid.*, **504**, 131, (1933).

Table 2  
*Some Simple Equilibria in the Gaseous Phase*

Reference	Equilibrium	<i>K</i>	<i>W</i>	$\Delta H^\circ$	$\Delta S^\circ$
(1)	$\text{Cl}_2 \rightleftharpoons 2\text{Cl}$	$[\text{Cl}]^2/[\text{Cl}_2]$	$4.90 \times 10^3$	57,500	16.9
(2)	$\text{Br}_2 \rightleftharpoons 2\text{Br}$	$[\text{Br}]^2/[\text{Br}_2]$	$2.78 \times 10^3$	46,100	15.8
(3)	$\text{I}_2 \rightleftharpoons 2\text{I}$	$[\text{I}]^2/[\text{I}_2]$	$1.13 \times 10^3$	33,900	14.0
(4)	$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$	$[\text{NO}]^2/[\text{N}_2][\text{O}_2]$	$4.27 \times 10^1$	43,100	7.5
(5)	$2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$	$[\text{NO}]^2[\text{O}_2]/[\text{NO}_2]^2$	$4.54 \times 10^6$	29,200	30.5
(6)	$\text{SbCl}_5 \rightleftharpoons \text{SbCl}_3 + \text{Cl}_2$	$[\text{SbCl}_3][\text{Cl}_2]/[\text{SbCl}_5]$	$1.89 \times 10^5$	16,320	24.2
(7)	$2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$	$[\text{H}_2][\text{I}_2]/[\text{HI}]^2$	0.18	2,940	-3.4

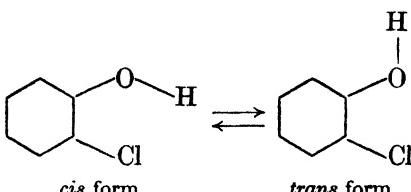
- (1) Wohl and Kadow, *Z. physikal. Chem.*, **118**, 460, (1925).
- (2) Bodenstein, *Z. Elektrochem.*, **22**, 327, (1916).
- (3) Bodenstein and Stark, *ibid.*, **16**, 961, (1910); Braune and Ramstetter, *Z. physikal. Chem.*, **102**, 480, (1922).
- (4) Briner, Bauer, and Rothen, *J. Chim. Phys.*, **23**, 788, (1926); *Helv. Chim. Acta*, **9**, 634, (1926); *Tables Annuelles*, **7**, 1244, (1930).
- (5) Raschig and Prahl, *Z. angew. Chem.*, **42**, 253, (1929).
- (6) Braune and Tiedje, *Z. anorg. Chem.*, **152**, 39, (1926).
- (7) Bodenstein, *Z. physikal. Chem.*, **29**, 295, (1899); Stegmüller, *Z. Elektrochem.*, **16**, 85, (1910).

are simple ones, containing only a few atoms each, it is also possible to calculate  $\Delta S^\circ$  from the statistical treatment of the gaseous system, assuming the ideal gas laws, and using spectroscopic constants for the internuclear distances and intramolecular vibrations. Without enlarging on these matters, however, there are some useful conclusions which may be drawn directly from an inspection of Table 2. In the first place, when we consider a series of equilibria of the same type, for example, the atomization of the halogen molecules ( $X_2 \rightleftharpoons 2X$ ), we see that the great differences in the values of *K* for various members of the series are chiefly due to differences in the energies required to dissociate the molecules, and are only in the second degree dependent on the term  $\Delta S^\circ$ . Secondly, the standard increase in entropy is small when the equilibrium to which it refers is a symmetrical one, in the sense that there is little configurational difference between reactants and resultants. Finally, large values of  $\Delta S^\circ$  are always to be found when the number of molecules is different from the number formed, i.e. when the stoichiometric equation is unbalanced, and particularly when there is a marked difference in the chemical character of the reactants and products. These generalizations can be mathematically formulated in simple cases, but they are equally true even when it is not possible to find mathematical expressions for them.

*Equilibria in Solution*

More varied results await us when we turn our attention to equilibria in solution—a subject which is being studied by many very different methods. The most thoroughly investigated equilibria are ionizations in water, which are discussed in a later section (p. 191). Here we confine ourselves to other types of balanced reactions, chiefly in non-polar solvents. In view of the great wealth of material recently made available, we must content ourselves with representative examples, ranging from the finely adjusted equilibria set up between configurationally distinguishable modifications of a single compound to the more robust kind of balance set up between reactants and products of widely different chemical character. Two intermediate types of equilibria, of considerable kinetic consequence, must also be examined. One refers to the state of aggregation of solute molecules in solution, and the other to the peculiarities attending the union of two molecules into a complex molecule.

The characteristic frequency of the —O—H group, as revealed by the absorption of light by molecules containing it, is characteristic only in so far as no atoms other than the carbon and hydrogen atoms of the normal paraffin chain interfere with the vibration. If another atom is held near to the —O—H group, as in *o*-substituted phenols, the intensity and position of the infra-red absorption band are both influenced; and from the variation of the intensity with respect to temperature, it is possible to calculate the difference between the energy of the freely rotating hydrogen atom in the hydroxyl group and its energy when clamped. In this way, M. M. Davies† has shown that the conversion of *cis*-*ortho*-chlorphenol to the *trans* modification



is associated, in carbon tetrachloride solution, with an increase in energy of 1.4 kilocalories per gram molecule, in agreement with a value of 1.8 which was anticipated on theoretical grounds. Similar results have been found‡ for the *cis* and *trans* equilibria of chloral

† *Trans. Faraday Soc.*, 34, 1427, (1938).

‡ *Idem, ibid.*, 36, 393, (1940).

hydrate,  $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$ , and of bromal hydrate. If one of these forms were more disposed than its isomer to react with a common reagent, the difference between the energies of activation of the two reactions would be of this order of magnitude, and the effect of the configurational equilibrium on the relative rates would not be a great one. The subject, however, is not one that should be lightly dismissed, for suppose that reaction were favoured by the simultaneous occurrence of a number of such preferable dispositions; we could expect a change of some 10,000 calories in the energies of activation. Contributory factors of this magnitude may well arise, for example, in the hydrolysis of carbohydrates.

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  to be found in Table 3 have been

*Table 3*  
*Certain Chemical Equilibria in Non-aqueous Solutions*

Reference	Reaction	Solvent	$\Delta H^\circ$ (kilo-cals./gm. mole)	$\Delta S^\circ$ (calories/gm. mole-degree)
(1)	$p\text{-BrC}_6\text{H}_4\text{NBr}(\text{CH}_3)_2\text{C}_6\text{H}_5$ $\rightleftharpoons$ $p\text{-BrC}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{Cl}_4$ $\text{CHCl}_3$ $\text{C}_6\text{H}_5\text{NO}_2$	19·1 18·9 15·0	59·7 59·5 36·9
(2)	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{I} \rightleftharpoons \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 + \text{CH}_3\text{I}$			18·5
(3)	$p\text{-BrC}_6\text{H}_4\text{NBr}(\text{CH}_3)_2\text{C}_6\text{H}_5$ $\rightleftharpoons$ $p\text{-BrC}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{C}_6\text{H}_5\text{Br}$	10 per cent. aq. $(\text{CH}_3)_2\text{CO}$	15·5	37·6
(4)	$p\text{-ClC}_6\text{H}_4\text{NBr}(\text{OH}_2)_2\text{C}_6\text{H}_5 \rightleftharpoons p\text{-ClC}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	7·7	20·8
(5)	$(\text{C}_6\text{H}_5)_2\text{SBr} \rightleftharpoons (\text{C}_6\text{H}_5)_2\text{S} + \text{C}_6\text{H}_5\text{Br}$	$\text{H}_2\text{O}$	26·7	9·6
(6)	$\text{R}_3\text{C}(\text{OH})\text{CN} \rightleftharpoons \text{R}_3\text{CO} + \text{HCN}$	$\text{C}_6\text{H}_5\text{OH}$ " " $\text{CHCl}_3$ $\text{CHCl}_2$ , $\text{C}_6\text{H}_5$ , $\text{CS}_2$	28·1 24·2 28·1 15·6	10·4 8·4 9·1 23·4
(7)	$(\text{C}_6\text{H}_5)_2\text{C} - \text{C}(\text{C}_6\text{H}_5)_2 \rightleftharpoons 2\text{C}(\text{C}_6\text{H}_5)_2$	$\text{CHCl}_3$ , $\text{C}_6\text{H}_5$ , and $\text{C}_6\text{H}_11$	10·1	26·3
(8)	$\text{R}(\text{C}_6\text{H}_5)_2\text{C} - \text{C}(\text{C}_6\text{H}_5)_2\text{R} \rightleftharpoons 2\text{R}(\text{C}_6\text{H}_5)_2\text{C}$	Pure liquid	-3·4	-95·5
(9)	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	Pure liquid	8·2	32·7
(10)	$\text{CH}_3\text{CO}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COCH}_3 \rightleftharpoons 2(\text{CH}_3)_2\text{CO}$			

- (1) von Halban, *Dissertation*, Würzburg, (1909); *Z. physikal. Chem.*, **67**, 129, (1909); *ibid.*, **77**, 719 (1911).
- (2) Essex and Gelormini, *J. Amer. Chem. Soc.*, **48**, 882, (1920).
- (3), (4) W. C. Davies and R. G. Cox, *Trans. Chem. Soc.*, 614, (1937).
- (5) Corran, *Trans. Faraday Soc.*, **23**, 605, (1927).
- (6) T. D. Stewart and B. J. Fontana, *J. Amer. Chem. Soc.*, **62**, 3281, (1940).
- (7) Ziegler, *Trans. Faraday Soc.*, **30**, 10, (1934); Ziegler and Ewald, *Annalen*, **473**, 163, (1929).
- (8) Wooster, *J. Amer. Chem. Soc.*, **58**, 2156, (1936).
- (9) Glockler and Peck, *J. Chem. Physics*, **4**, 659, (1926).
- (10) Darvis and Burrows, *J. Amer. Chem. Soc.*, **58**, 311, (1936).

calculated from equilibrium constants determined at various temperatures, and relate to equilibria of the more usual chemical type. von Halban's early work on the Menschutkin equilibria has been in the main confirmed in a careful reinvestigation by W. C. Davies and

J. Cox, who have shown that the alternative modes of decomposition of the quaternary ammonium salt are not appreciably followed, and that, due to slow interaction of the alkyl halide with the solvent, probably all equilibria of this type are false ones in hydroxylic media. The same conclusion must apply to the decomposition and formation of sulphonium salts. An equally careful investigation of the conditions governing the formation of cyanohydrins, by T. D. Stewart and Fontana, has indicated that the familiar mechanism first proposed by Lapworth is strictly applicable only to aqueous solutions. The estimates of the strength of the carbon–carbon bond in the various tetraphenyl ethanes show considerable uniformity, and a genuine difference from the value computed (p. 167) for hexaphenylethane.

#### *A Classification of Equilibrium Systems in Solution*

We have now to deal briefly with the remaining types of equilibria in the scheme:

- (1) Configurational equilibria,
- (2) Chemical equilibria,
- (3) Dimerization,
- (4) Complex formation,
- (5) Ionization,

which is based primarily on the order of their increasing significance to chemical kinetics.

#### *Dimerization in Solution*

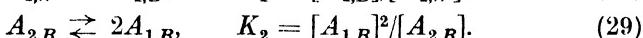
As Nernst first showed,† fatty acids exist chiefly as double molecules in non-polar solvents. Nernst, in fact, considered them to exist solely as double molecules, but more recent work has shown that this supposition is not quite true. The percentage of the total acid which is present as single molecules is as low as 2·5 per cent. at 0° C., and increases to about 15 per cent. at 70° C. These figures refer to acetic acid in benzene solution, and were obtained by the following means from experiments on the distribution of the acid between water and benzene at various temperatures.‡

Let the acetic acid molecule be denoted by *A*, and its monomeric and dimeric forms by the subscripts 1 and 2 respectively. The subscripts *W* and *B* refer to the solvents, water and benzene,

† *Z. physikal. Chem.*, **8**, 110, (1891).

‡ *Trans. Chem. Soc.*, **850**, (1940).

respectively. The partial ionization in aqueous solution can be neglected. We have then the following equilibria to consider:



It follows that the ratio,  $c_B/c_W$ , of the total concentrations of acetic acid in the benzene and water layers is

$$\frac{c_B}{c_W} = K_1 + \frac{2K_1^2}{K_2} c_W. \quad (30)$$

The observed partition ratio should therefore increase linearly with the total concentration of solute in the aqueous layer. The intercept corresponding to a zero aqueous concentration yields the first equilibrium constant; and from the gradient the second equilibrium constant may be evaluated. An illustration of the applicability of this relation is given in Table 4. Using the original assumption of

Table 4

*The Distribution of Acetic Acid between Water and Benzene  
(concentrations in gram molecules per litre)*

$T = 318.17^\circ \text{ K}$ .  $K_1 = 1.39 \times 10^{-2}$ ;  $K_2 = 1.62 \times 10^{-2}$

$c_B$	$c_W$	$100c_B/c_W$ (observed)	$100c_B/c_W$ (by equation (30))
0.0042	0.222	1.87	1.90
0.0109	0.442	2.46	2.43
0.0192	0.649	2.97	2.92
0.0294	0.857	3.43	3.42
0.0415	1.068	3.89	3.92

complete dimerization, we clearly obtain the distribution law of Nernst,

$$\sqrt{(c_B)/c_W} = K, \quad (31)$$

in which  $K = K_1(2/K_2)^{\frac{1}{2}}$ . The influence of temperature on both equilibrium constants is adequately summarized by equation (26), with the specific values

$$\Delta S_1^0 = 7.15 \text{ cal./gm. mol.-deg.}, \quad \Delta H_1^0 = 4,980 \text{ cal./gm. mol.},$$

$$\Delta S_2^0 = 22.32 \text{ cal./gm. mol.-deg.}, \quad \Delta H_2^0 = 9,700 \text{ cal./gm. mol.}$$

Experimental values and those produced by these formulae are compared in Table 5. A spectroscopic investigation of the same dimerization in carbon tetrachloride solution† had previously afforded the value of  $9.3 \pm 1$  kilocalories for  $\Delta H_2^0$ , with which the later result

† M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Physics*, **6**, 755, (1938).

agrees well. The nature of the infra-red absorptiometric method, like the colorimetric method, makes it impossible to estimate  $\Delta S^\circ$  at all accurately.

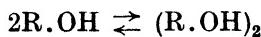
Table 5

*Determination of the Dimerization Energy of Acetic Acid in Benzene, and the energy of Transfer of Single Molecules from Benzene to Water*

$T, {}^\circ\text{K.}$	$K_1 \times 10^3$		$K_2 \times 10^3$	
	Observed	By equation (26)	Observed	By equation (26)
290.14	6.4	6.51	4.0	3.73
297.23	8.0	7.98	5.6	5.57
298.18	8.2	8.18	6.0	5.88
303.56	9.5	9.50	7.8	7.85
307.82	10.8	10.64	9.8	9.77
318.17	13.9	13.86	16.2	16.40
335.11	20.6	20.68	36.1	35.70

Earlier experiments on the distribution of acetic acid and benzoic acid between water and a variety of solvents, including carbon disulphide, carbon tetrachloride, and benzene, when analysed in the light of equation (30), afford additional confirmation of its validity, and lead to values of  $K_2$  at 298.1° K. differing by a factor of not more than 3 from that obtained by the later work.† In chloroform solution, however,  $K_2$  is about 24 times as great.‡ With the chloracetic acids dissolved in *p*-chlortoluene, the mutual attachment of the solute molecules is so great that monomers cannot be detected by the cryoscopic method.§  $\Delta H^\circ$  for the dimerization of gaseous acetic acid is  $14,500 \pm 400$  cals. per gram. mole of double molecules.||

An ingenious method has been used by von Elbe†† to determine the energy released when two molecules of a normal alcohol form a bimolecular complex. It is based on the assumption that the pure liquid alcohol consists entirely of dimeric molecules, and on an analysis of the vapour pressures and heats of dissolution of the alcohols in an inert solvent. von Elbe concludes, from the functional relationship which exists between the extent of polymerization and the heat of dilution that the reaction



† Herz and Kurzer, *Z. Elektrochem.*, **16**, 869, (1910); Nernst, *loc. cit.*

‡ Rothmund and Wilsmore, *Z. physikal. Chem.*, **40**, 611, (1902).

§ R. P. Bell, Baughan, and Vaughan-Jackson, *Trans. Chem. Soc.*, 1969, (1934).

|| Ritter and Simons, *J. Amer. Chem. Soc.*, **67**, 761, (1945).

†† *J. Chem. Physics*, **2**, 73, (1934); cf. Wohl, Pahlke, and Wehago, *Z. physikal. Chem.*, **B**, **28**, 1, (1935).

is accompanied by a decrease in heat content of 11.6 kilocalories, and that this value is common to all normal alcohols in all normal hydrocarbons. Dimers formed from aryl halides are less stable:  $\Delta H^0$  for the dimerization of phenyl halides in carbon tetrachloride solution ( $2A \rightleftharpoons A_2$ ) varies from  $-1.1$  to  $-1.7$  kilocalories.<sup>†</sup> The rate at which reactions of the type  $RCl + CH_3OH \rightarrow ROCH_3 + HCl$  proceed in nitrobenzene solution is given by the equation

$$v = k_2[RCl][CH_3OH] + k_3[RCl][CH_3OH]^2. \ddagger$$

The second term we can readily explain in terms of interaction of the halide with the alcohol dimer.

The distribution, spectroscopic, and calorimetric methods of investigating dimerization in solution give concordant results, and logically supplement the pioneer work on the union of such free radicals as 9-brom-phenanthroxy.<sup>§</sup> Some typical values of  $\Delta H^0$  and  $\Delta S^0$  for reactions of this type, calculated from the equilibrium data of Goldschmidt and Bader<sup>||</sup> are given in Table 6.

Table 6

*The Formation of Free Radicals in Solution. Reaction  $A_2 \rightleftharpoons 2A$ , where A is  $\alpha\alpha'$ -diphenyl-p-benzoyl hydrazyl*

Solvent	$\Delta H^0$ (kilocals./gm. mole)	$\Delta S^0$ (calories/gm. mole-deg.)
CHCl <sub>3</sub>	5.2	9.5
(CH <sub>3</sub> ) <sub>2</sub> CO	6.8	3.5
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	10.5	2.4
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O	9.4	-0.1

### Complex Formation in Solution

Addition compounds formed from neutral, un-ionized molecules in solution now appear, despite the scepticism that has long existed about them, to be the rule rather than the exception. They are generally formed from polar molecules, and are most stable in inert solvents, as one would expect if their existence is due to the mutual attraction of dipoles. The well-known coloured complexes often formed from nitro-compounds and hydrocarbons probably have a similar origin. They are less stable than the dipole-dipole complexes, and not yet so fully understood.

<sup>†</sup> Sakurada, *Z. physikal. Chem.*, **28B**, 104, (1935).

<sup>‡</sup> Bartlett and Nebel, *J. Amer. Chem. Soc.*, **62**, 1345, (1940).

<sup>§</sup> Goldschmidt, Vogt, and Bredig, *Annalen*, **445**, 123, (1925).

<sup>||</sup> *Ibid.*, **473**, 137, (1929).

Many physicochemical methods have been employed to elucidate the nature of these intermediate complexes since Behrends† first applied the laws of chemical equilibrium to the problem. The presence of the complex in solution is sometimes attended by the appearance of as many as four new Raman frequencies which are not present in the solutions of either reactant. This is the case, for example, in the complex formed from hydrogen bromide and diethyl ether.‡ When one of the molecules forming the complex is initially non-polar, it is found from polarization measurements that in the complex formed it has lost its symmetry.§

Generally, when a complex is formed between two solutes, its presence is indicated by the departure of the properties of the solution from those which we are entitled to expect if the solutes do not interact. Among the properties thus used may be listed the density,|| vapour pressure,†† specific heat,†† solubility,§§ dielectric constant,|||| and viscosity.†††

The most accurate results hitherto obtained are those of Magdin and his collaborators,††† who have used the cryoscopic method to obtain the equilibrium constant of the equation,

$$K = a_{AB}/a_A a_B, \quad (32)$$

in terms of the activities,  $a$ , and the activity coefficients,  $\gamma$ . A set of typical results is shown in Table 7, the first column of which gives the molar ratio,  $M$ , of *p*-toluidine to *p*-chlorphenol. In the second column is to be found the depression of the freezing-point of the solvent, benzene, and in the last column the equilibrium constant,  $K$ . Similar values have been determined by the same workers for numerous systems of aryl halides and nitrogen bases, forming complex molecules in benzene solution and in *p*-dichlorbenzene solution: the temperature range covers about 50° C.

† *Z. physikal. Chem.*, **15**, 183, (1894).

‡ Briegleb and Lauppe, *ibid.*, **B**, **28**, 154, (1935).

§ Ulich, *Z. angew. Chem.*, **44**, 750, (1931).

|| Bramley, *Trans. Chem. Soc.*, **109**, 11, 434, (1916).

†† Schultze, *Z. physikal. Chem.*, **86**, 309, (1914).

†† McLeod and F. J. Wilson, *Trans. Faraday Soc.*, **31**, 596, (1935).

§§ Ley and Grau, *Berichte*, **58 B**, 1765, (1925).

|||| Earp and Glasstone, *Trans. Chem. Soc.*, **1709**, (1935).

††† McLeod, *Trans. Faraday Soc.*, **30**, 482, (1934); see also Drucker, *Z. physikal. Chem.*, **92**, 309, (1918).

††† Glass and Magdin, *Trans. Chem. Soc.*, **193**, (1933); **1431**, (1933); **261**, (1934); **1292**, (1934); Burnham and Magdin, *ibid.*, **606**, (1937).

Table 7

*Equilibrium Constants ( $K = a_{AB}/a_A a_B$ ) for the Union of *p*-Toluidine (*A*) and *p*-Chlorophenol (*B*) at Various Molar Ratios in Benzene Solution*

$10^3 M$	$\Delta T^\circ$	$\gamma_A$	$\gamma_B$	$\gamma_{AB}$	$K$
0.525	0.068	1.000	0.996	0.998	47.47
0.815	0.105	0.997	0.994	0.994	48.32
1.619	0.204	0.994	0.990	0.988	48.10
2.332	0.289	0.993	0.984	0.957	48.39
4.556	0.534	0.987	0.970	0.885	48.97
5.203	0.601	0.986	0.968	0.825	49.01
6.155	0.697	0.985	0.962	0.786	47.96
6.846	0.764	0.984	0.960	0.761	49.02
9.040	0.967	0.981	0.953	0.691	48.19
10.28	1.073	0.979	0.948	0.650	48.88
11.33	1.160	0.977	0.941	0.624	48.04
13.19	1.310	0.975	0.935	0.600	48.55
16.00	1.528	0.973	0.930	0.551	48.25
18.24	1.697	0.971	0.928	0.525	48.66
20.21	1.838	0.969	0.926	0.505	48.10
22.08	1.978	0.968	0.924	0.489	47.84
24.51	2.144	0.967	0.920	0.475	48.16
27.04	2.316	0.965	0.914	0.462	47.80
30.47	2.560	0.963	0.910	0.447	48.76
32.56	2.704	0.961	0.908	0.437	48.69
38.44	3.096	0.959	0.900	0.422	49.03
41.37	3.296	0.958	0.898	0.417	48.98
44.39	3.500	0.956	0.891	0.412	48.81

Average value of  $K$ : 48.39.

Values of  $\Delta H^\circ$  and  $\Delta S^\circ$  calculated from these constants, and from some representative investigations of earlier workers, have been summarized in Table 8.

#### *The Computation of Complex Stability in Solution*

We shall need, in the next chapter, some information on the energy released when a complex is formed in solution but for which no direct measurements have yet been made.

When the force attracting two molecules in a solvent of dielectric constant,  $D$ , is due to the electrostatic interaction of two dipoles, of moments  $\mu_A$  and  $\mu_B$ , we may, for a linear arrangement, express the total interaction energy as follows:<sup>†</sup>

$$u = Aa^{-9} - Ba^{-3}. \quad (33)$$

Here,  $A$  is a repulsion constant, and  $a$  the distance apart of the dipoles.

<sup>†</sup> See Mie, *Annalen der Physik*, 11, 657, (1903), who has used this equation in connexion with another problem; and Lennard-Jones, in Chapter X of Fowler's *Statistical Mechanics*, for a general treatment of intermolecular forces.

Table 8

Complex Formation in Solution ( $AB \rightleftharpoons A + B$ ;  $K = a_A a_B / a_{AB}$ )

Reference	<i>A</i> and <i>B</i>	Solvent	$\Delta H^\circ$ (kilocalcs./gm. mole)	$\Delta S^\circ$ (calories/gm. mole-degree)	Method
(1)	$1:3:5-(NO_2)_2C_6H_4 + C_6H_5N(C_6H_5)_2$	$CHCl_3$	4.9	10.6	Photometric
	$1:3:5-(NO_2)_2C_6H_4 + p-CH_3C_6H_4N(C_6H_5)_2$	$CHCl_3$	2.1	9.5	Ebulloscopic
(2)	$o-ClC_6H_4OH + p-CH_3C_6H_4NH_2$	$C_6H_6$	3.5	5.05	Cryoscopic
	$p-ClC_6H_4OH + p-CH_3C_6H_4NH_2$	$C_6H_6$	4.2	5.25	
(3)	$p-ClC_6H_4OH + C_6H_5N$	$C_6H_6$	6.8	13.9	
	$CHCl_3 + (CH_3)_2CO$	Pure liquids	4.1	12.4	Vapour pressure
(4)	$CHCl_3 + (C_6H_5)_2O$	Pure liquids	6.0	3.0	Calorimetric
	$C_{10}H_8 + 1:3:5-(NO_2)_2C_6H_5OH$	$CCl_4$	0.7	5.7	Spectrometric
(5)	$C_{10}H_8 + 1:3:5-(NO_2)_2C_6H_5$	$CCl_4$	2.7	5.5	
	$C_{10}H_8 + m-(NO_2)_2C_6H_4$	$CCl_4$	1.5	7.4	

(1) Ley and Grau, *loc. cit.*(2) Burnham, Glass, and Magdin, *loc. cit.*(3) Schultz, *loc. cit.*(4) McLeod, *loc. cit.*(5) von Halban and Zimpelmann, *Z. physikal. Chem.*, **117**, 461, ( 925).  $K$  in litres per gram molecule.

On the basis of a discussion given in Chapter VII, we adopt, for the attraction constant, the expression

$$B = 2\mu_A \mu_B \left( \frac{D+2}{3D} \right). \quad (34)$$

The distance apart,  $a_0$ , of the dipoles in their most stable state, and the energy,  $u_0$ , of the pair in that state are found, from the equilibrium condition,  $du/da = 0$ , to be given by the relations

$$a_0^6 = 3A/B \quad (35)$$

and  $-u_0 = \frac{2B}{3a_0^3}, \quad (36)$

whence, by elimination, the repulsion constant becomes

$$A = \frac{4}{27} \frac{B^3}{u_0^6}. \quad (37)$$

On applying these formulae to the interaction of pyridine ( $\mu = 2.16 \times 10^{-18}$ ) and *p*-chlorphenol ( $\mu = 2.25 \times 10^{-18}$ ) in benzene solution, for which  $(D+2)/3D$  is 0.6464, we find that  $B$  is  $6.28 \times 10^{-36}$  erg-cm.<sup>3</sup> From the cryoscopic work of Magdin and his collaborators (Table 8),  $-u_0$  in the case of this complex is seen to be  $4.7 \times 10^{-13}$  erg/pair. By means of equations (34) and (37), the numerical value of the repulsion constant becomes

$$A = 1.66 \times 10^{-82} \text{ erg-cm.}^3$$

It is noteworthy that this estimate from freezing-point data in solution should be in such close proximity to the value ( $3.5 \times 10^{-82}$ ) found for the repulsion constant between two neon atoms from the virial coefficients of the gas (Lennard-Jones, *loc. cit.*, p. 306).

We can now use this value of  $A$  to determine the properties of other complexes of the same type, in which the chief source of repulsion arises from the electronic octets in the carbon and nitrogen atoms, such, for example, as that formed between pyridine and methyl iodide ( $\mu = 1.41 \times 10^{-18}$ ) in the same solvent.  $B$  now becomes  $3.95 \times 10^{-36}$ , and

$$a_0 = 2.24 \times 10^{-8} \text{ cm.},$$

while  $-u_0 = 3,385 \text{ cals./mole.}$

The intermolecular frequency of vibration can readily be shown to be

$$v_0 = \frac{3}{2\pi a_0} \sqrt{\frac{3|-u_0|}{m^*}}, \quad (38)$$

where  $m^*$  is the reduced mass. The numerical value for the pyridine-methyl iodide complex is thus found to be  $1.96 \times 10^{12} \text{ sec.}^{-1}$

### *The Solubility of Gases in Liquids*

The solubility of some compounds, expressed as a molar fraction,  $N$ , of the solute in the liquid phase, is found to be equal to the ratio of the partial pressure,  $p$ , of the solute, in the vapour phase in equilibrium with the solution, to the vapour pressure,  $p^0$ , of the solute as a pure liquid at the same temperature:<sup>†</sup>

$$N = p/p^0. \quad (39)$$

Only in a relatively small number of cases, however, have the experimental data been presented in this form. Most of the solubilities of interest to us have been given in terms of concentrations, the unit of which has usually been the gram molecule per litre. The Ostwald absorption coefficient,  $s$ , for example, is the ratio of the concentration,  $c_s$ , of the solute in solution, to the concentration,  $c_g$ , of the solute in the vapour phase with which the solution is in equilibrium:

$$s = \frac{c_s}{c_g}. \quad (40)$$

It is not difficult to transform one of these laws into the other when

† Raoult, *Z. physikal. Chem.*, **2**, 353, (1888).

both the vapour and the solution are dilute, for, under such conditions, the partial pressure of the vapour of the solute is

$$p = RTc_s, \quad (41)$$

and its molar fraction,  $N$ , in solution, is very nearly

$$N = (V_s/1000)c_s. \quad (II\ 22)$$

Here,  $V_s$  is the molar volume of the solvent. On comparing these relations, we see that

$$s = 1000 \frac{RT}{p^0 V_s}. \quad (42)$$

Ostwald's constant,  $s$ , is an equilibrium constant—the first one which we have had to deal with in a heterogeneous system. So long as the pressure of the system, vapour plus liquid, is maintained constant, as it usually is, there is no objection to our applying to it the familiar isochore of van 't Hoff (equation (23)):

$$\Delta H^0 = RT^2 \left( \frac{d \ln s}{dT} \right)_P. \quad (43)$$

It is clear that  $-\Delta H^0$  denotes the excess of heat content possessed by one mole of solute vapour over the heat content of one mole of solute in solution at the same temperature and pressure. On applying this relation to the solubilities, at various temperatures, of argon in water, we obtain, from different sources, the following values for  $-\Delta H_{298.1}^0$ : 2,114,<sup>†</sup> 2,143,<sup>‡</sup> and 2,070<sup>§</sup> calories per gram mole. The experimental data for helium,<sup>§</sup> neon,<sup>§</sup> krypton,<sup>||</sup> xenon,<sup>||</sup> and radon<sup>††</sup> have been examined in the same way, with results which are summarized in the fourth column of Table 9. The error in  $\Delta H_{298.1}^0$ , as far as it can be estimated, increases from about 40 calories for argon, to about 240 calories for radon. From these values, we may use equation (26) or (27) to determine other thermodynamic properties, such as the change in the standard entropy during dissolution (column 5). The entropy of one gram mole of an inert gas,  $S_g^0$ , at this temperature and at a concentration of one gram mole per litre in the gaseous phase can be readily calculated from first principles. The results are given

<sup>†</sup> Streicher, *ibid.*, **31**, 176, (1899).

<sup>‡</sup> Winkler, *ibid.*, **55**, 344, (1906).

<sup>§</sup> Lannung, *J. Amer. Chem. Soc.*, **52**, 68, (1930).

<sup>||</sup> Schulze, *Z. physikal. Chem.*, **95**, 257, (1920).

<sup>††</sup> Rammstedt, *Le Radium*, **8**, 253, (1911); Rutherford, *Radioactive Substances and their Radiations*, p. 377, Cambridge, (1913); Valentiner, *Z. physikal. Chem.*, **42**, 253, (1927).

in column 6 of Table 9. The standard molar entropies of these solutes in water at 25° C., obtained from the relation

$$\Delta S^0 = S_s^0 - S_g^0, \quad (44)$$

are given in column 7. The concentration to which the entropy refers, in solution as in the gaseous phase, is one gram molecule per litre.

*Table 9*

*The Solubility of the Inert Gases in Water ( $s = c_s/c_g$ )*

(All the figures refer to 298.1° K. and a total pressure of 1 atmosphere)

Gas	$s \times 10^3$	$\Delta G^0$	$\Delta H^0$	$\Delta S^0$	$S_g^0$	$S_t^0$	$L$ (calories/ gram mole)
		(calories/gm.-m.)		(calories/ gram mole-degree)			
He	9.47	2,760	0	- 9.3	23.8	14.5	23
Ne	11.1	2,660	- 320	- 10.0	28.6	18.6	413
A	34.7	2,000	- 2,110	- 13.8	30.6	16.8	1,500
K <sub>1</sub>	39.6	1,910	- 2,870	- 16.0	32.8	16.8	2,314
X	120.0	1,260	- 3,460	- 15.8	34.2	18.4	3,210
Rn	218.0	900	- 4,030	- 16.6	35.8	19.2	4,340

On differentiating the right-hand side of equation (42) with respect to temperature, and on multiplying the result by  $RT^2$ , we obtain another expression for the increase in heat content attending dissolution, viz.

$$\Delta H^0 = -L + RT(1-\alpha T). \quad (45)$$

$L$  is the latent heat of vaporization of the pure solute, and  $\alpha$  is the coefficient of cubical expansion of the solvent. As a rule only  $L$  is important.† According to this equation, the energy which a molecule carries with it on vaporizing is the same as the energy it takes with it on dissolving in a solution which obeys Raoult's law (equation (39)). That this is true in a general way for the inert elements dissolving in water is readily seen from an inspection of Table 9, the last column of which contains the heats of vaporization of the liquid elements.‡ It is not without significance that the increase in standard entropy associated with vaporization at the boiling-point, which increases as we ascend the periodic series, should be paralleled by the increase in standard entropy attending dissolution in water. These facts indicate

† In an earlier derivation (*The Kinetics of Reactions in Solution*, 1st ed., p. 143, (1933)), the term  $RT(1-\alpha T)$ , which amounts to 375 calories per mole in the case of carbon tetrachloride at 25° C., was not included, as it has been in later derivations. Cf. Bell, *Trans. Faraday Soc.*, **33**, 436, (1937); Guggenheim, *ibid.*, **33**, 613, (1937).

‡ Moelwyn-Hughes, *Physical Chemistry*, Cambridge, p. 354, (1940).

that the field of force surrounding the inert gas molecule in water is not widely different from that which surrounds it in the pure liquid. Actually, the values of  $L$  are, on the whole, less than the values of  $-\Delta H^0$ , but the reason is neither the inadequacy of the treatment, nor the omission of trivial factors such as  $RT(1-\alpha T)$ , but that  $\Delta H^0$ , as measured experimentally, increases with an increase in temperature. The values of  $d(\Delta H^0)/dT$  vary from 40 calories/mole-degree in the case of neon to 100 in the case of radon. Better agreement, in other words, would have been obtained if we had used values of  $-\Delta H^0$  at lower temperatures.

When there is no proportionality between the partial pressure and the molar fraction of the solute, the laws of solubility become more complicated and are as yet only dimly understood.

It is interesting to note that complex formation between solute and solvent is among the principal hypotheses enlisted to explain the abnormalities.†

### *The Influence of Solvents on Chemical Equilibrium*

The dissolution of a gas, a liquid, or a solid in a solvent is generally associated with a change in energy, so that, as a rule, the presence of a solvent may be expected to alter the position of a chemical equilibrium reached in it. When the total energy gained by the reactants on dissolving exactly balances the total energy gained by the resultants on dissolving, we have the special case of an inert solvent, that is, one which is without apparent effect on chemical equilibrium. To formulate these generalizations more precisely, we may consider the reaction



to attain equilibrium in the gaseous phase at constant temperature and pressure. The equilibrium constant, expressed in terms of partial pressures, is

$$K_g = \frac{p_B p_C}{p_A}. \quad (46)$$

Let the equilibrium constant,  $K_m$ , for the same reaction, at the same temperature and pressure, but in solution, be expressed in terms of the molar fractions,  $N$ , of the various solutes:

$$K_m = \frac{N_B N_C}{N_A}. \quad (47)$$

† Hildebrand, *The Solubility of Non-Electrolytes*, 2nd ed., Reinhold Publishing Co., New York, (1936).

Denoting by  $N_s$  the total number of gram moles of solvent, and by  $N_A$ ,  $N_B$ , and  $N_C$  the total numbers of gram moles of solutes in the solution, the molar fraction of  $A$  is

$$N_A = \frac{N_A}{N_A + N_B + N_C + N_s}. \quad (48)$$

Similar expressions apply to the three other components. The ratio of the equilibrium constants in the two phases at equilibrium is thus

$$\frac{K_g}{K_m} = \frac{(p_B/N_B)(p_C/N_C)}{(p_A/N_A)}. \quad (49)$$

If the solution obeys Raoult's law, we have, for each solute:

$$p/N = p^0, \quad (50)$$

so that  $K_g/K_m = \frac{p_B^0 p_C^0}{p_A^0}, \quad (51)$

or, in general,  $K_g/K_m = \frac{\prod_j p_j^0}{\prod_i p_i^0}. \quad (52)$

The product of the vapour pressures in the denominator is for all the  $i$  reactants, and in the numerator for all the  $j$  resultants. By applying the van't Hoff isochore (equation (23)), we thus obtain, in the special case,

$$\Delta H_g^0 - \Delta H_m^0 = L_B + L_C - L_A, \quad (53)$$

and in the general case

$$\Delta H_g^0 - \Delta H_m^0 = \sum_j L_j - \sum_i L_i. \quad (54)$$

We have thus shown that, when solutions obey Raoult's law, the difference between the heats of reaction in the gas phase and in solution is equal to the difference in the algebraic sum of the heats of vaporization of the reactants and resultants. This law, though it has not apparently been directly verified, has, as we shall see, sometimes been used in computing from solubility data the difference between the heats of reaction in the gaseous phase and in solution.

Chemical equilibrium constants, especially in non-hydroxylic solvents, have, like solubilities, been usually expressed in concentrations, the unit of which is the gram molecule per litre:

$$K_c = \frac{c_B c_C}{c_A}. \quad (55)$$

By using equation (22) of Chapter II, we can relate the two constants, obtaining, in our special example,

$$\frac{K_c}{K_m} = \frac{1000}{V_s}, \quad (56)$$

and in general

$$\frac{K_c}{K_m} = \left( \frac{1000}{V_s} \right)^{\sum j - \sum i} \quad (57)$$

As in the preceding section,  $V_s$  stands for the molar volume of the solvent. Hence, proceeding as in the solubility problem, we obtain the following relation:

$$\Delta H_c^0 - \Delta H_m^0 = -(\sum j - \sum i)RT^2\alpha. \quad (58)$$

Eliminating  $\Delta H_m^0$  from equations (54) and (58), we arrive at the following connexion between the increase in heat content measured for a reaction in dilute solution and the corresponding quantity measured for the reaction in the gaseous state:

$$\Delta H_g^0 - \Delta H_c^0 = \sum_j L_j - \sum_i L_i + (\sum j - \sum i)RT^2\alpha. \quad (59)$$

Ignoring the correction for solvent expansion (p. 180), which is generally smaller than the experimental error, we obtain, for the particular reaction under examination:

$$\Delta H_g^0 - \Delta H_c^0 = L_B + L_C - L_A. \quad (60)$$

We are now in a position to discuss some experimental facts relating to the influence of solvents on chemical equilibria.

(i) *The Dissociation of Nitrogen Tetroxide*:  $N_2O_4 \rightleftharpoons 2NO_2$ . From Natanson's vapour density measurements at 0° C., it is found that the equilibrium constant for the gaseous dissociation is

$$K = [NO_2]^2/[N_2O_4] = 7.40 \times 10^{-4} \text{ gram molecules per litre.} \dagger$$

The colorimetric data of Cundall‡ yield, for the corresponding constant in chloroform solution,  $K = 5.70 \times 10^{-6}$ . In this solvent, therefore,  $K$  is about 130 times as small as it is in the gas phase—a difference the significance of which was realized by Ostwald.§ The relative velocities of the two reactions are thus altered to this extent, but whether the rate of dissociation or of combination or both is affected cannot be decided. The behaviour is in striking contrast with the decomposition of nitrogen pentoxide in these two systems.

† *Ann. Physik*, **27**, 606, (1886).

‡ *Trans. Chem. Soc.*, **59**, 1076, (1891).

§ *Ibid.*, **61**, 242, (1892).

Schreber,<sup>†</sup> from a review of numerous results, quotes 13,600 calories as the best value for the heat absorbed during the gaseous dissociation at constant pressure between 0° and 100° C. This figure is in good agreement with the value calculated by van 't Hoff<sup>‡</sup> and, more recently, by Giauque and Kemp, which is 13,693.<sup>§</sup> The effect of temperature upon the dissociation equilibrium in various solvents has been extensively examined by Cundall,<sup>||</sup> from whose results the following figures have been calculated.

Table 10

Solvent	$K_{20^\circ\text{C}}$ (gram molecules/litre)	$\Delta H_e^0$ (calories/gram mol.)	$\Delta H_e^0 - \Delta H_g^0$
Gas	382	13,690	0
SiCl <sub>4</sub>	17.8	20,470	6,780
CS <sub>2</sub>	13.3	19,400	5,710
CCl <sub>4</sub>	8.05	18,840	5,150
CHCl <sub>3</sub>	5.53	21,210	7,520
C <sub>2</sub> H <sub>5</sub> Br	4.79	20,490	6,800
C <sub>6</sub> H <sub>5</sub> Br and C <sub>6</sub> H <sub>5</sub> Cl	3.70	19,350	5,660
C <sub>6</sub> H <sub>6</sub>	2.23	22,180	8,490

Solutions of nitrogen tetroxide in chloroform are known to obey Raoult's law.<sup>††</sup> If the other solute and solvents obeyed the law, we would expect, from equation (56), a constancy in the product of  $K_c$  and the molar volumes,  $V_s$ , of the solvents. This is not the case.  $V_s$  is 114.5 c.c. in the case of silicon tetrachloride, and 70.6 c.c. in the case of benzene at 20° C. We therefore conclude that, either the other solute has an abnormal solubility or that Cundall's figures are in need of revision. The latent heat of vaporization of the tetroxide is 9,110 calories per gram mole.<sup>‡‡</sup> Using this figure in conjunction with the difference (7,520 calories) between the heats of reaction in the gas phase and in chloroform solution, we infer, from equation (60) that the molar heat of vaporization of nitrogen peroxide is 795 calories per mole, or about 100 calories less if allowance is made for the solvent expansion. The calorimetric datum is not known.

<sup>†</sup> *Z. physikal. Chem.*, **24**, 651, (1897).

<sup>‡</sup> *Studies in Chemical Dynamics*, p. 154, (1896).

<sup>§</sup> *J. Chem. Physics*, **6**, 40, (1938).

<sup>||</sup> *Trans. Chem. Soc.*, **67**, 794, (1895).

<sup>††</sup> Lewis and Randall, *Thermodynamics*, p. 303, McGraw-Hill Book Co., New York, (1923).

<sup>‡‡</sup> Giauque and Kemp, *loc. cit.*

(ii) *The Dissociation of Ethylene Iodide:*

This equilibrium has not been examined very carefully, but the results are of interest in spite of their approximate character. The constants for the gaseous reaction at temperatures of 11–65° C. have been determined by Mooney and Ludlam.† The total pressure of the system was measured statically, that of ethylene iodide by a streaming method, and that of iodine by difference. Under these conditions the value of  $K$  cannot refer to the homogeneous equilibria, as is borne out by the discontinuity observed at 40° C. in the curve found by plotting  $\ln K$  against  $1/T$ . Above this temperature the results are considered by the authors to be fairly trustworthy, and from the slope of the curve the heat of dissociation is found to be 22,300 calories. Scanty data for the corresponding equilibrium in carbon tetrachloride solution are also available, Polissar‡ finding  $\Delta H$  to be 11,300 calories in the neighbourhood of 137° C. These figures, despite a not considerable uncertainty, represent a genuine difference of about 10,000 calories in the thermal effects for the two systems. This difference, it is to be noted, is in a direction opposed to that found in the dissociation equilibrium discussed under section (i), and is about twice as great. In the light of equation (60) the result is understood as arising from the similarity in the heats of dissolution of ethylene and ethylene iodide in carbon tetrachloride, which thus nearly cancel out each other's effects, and in the relatively large magnitude of the heat of vaporization of iodine (*c.* 11,000 calories).

(iii) *The Dissociation of Ethane:*  $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$ . Benford and Wassermann§ have measured the solubility of these three gases in a variety of solvents in order to estimate, from equation (60), the solvent effect on the position of equilibrium. A summary of the results is given in Table 11.

As was to be expected, the solvent influence is not a great one. Although actually slightly higher than is indicated in the Table (because the experimental equilibria in the gas phase were expressed in terms of concentrations, and not by equation (46)), they are still very small compared with  $\Delta H_g^0$ , which is about 32,000 calories. Benford and Wassermann|| have also determined the values of  $W$

† *Proc. Roy. Soc. Edin.*, **49**, 160, (1929).

‡ *J. Amer. Chem. Soc.*, **52**, 956, (1930).

§ *Trans. Chem. Soc.*, **367**, (1939).

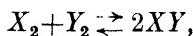
|| *Loc. cit.*

Table 11  
*The Influence of Various Solvents on the Dissociation of Ethane*

Solvent	$\Delta H_e - \Delta H_g$ (kilocalcs./gm. mole)
CCl <sub>4</sub>	-1.60
C <sub>6</sub> H <sub>6</sub>	-1.55
C <sub>6</sub> H <sub>5</sub> Cl	-1.33
CO(CH <sub>3</sub> ) <sub>2</sub>	-1.30
CH <sub>3</sub> COOCH <sub>3</sub>	-1.20

(equation (27)) for this reaction in the various solvents, and have shown that  $W_c/W_g$  is approximately unity for them all.

(iv) *Symmetrical Equilibria involving the Halogens.* An extremely painstaking investigation of the influence of a solvent on chemical equilibria is that of Blair and Yost† on highly symmetrical reactions of the type



in which  $X$  and  $Y$  stand for different halogen atoms. A summary of some of their results, referring to a temperature of 298.1° K., is given in Table 12.

Table 12  
*A Comparison of Various Equilibria in the Gaseous Phase and in Carbon Tetrachloride Solution*

Reaction	Medium	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$
$I_2 + Cl_2 \rightleftharpoons 2ICl$	Gas	-6,560	2.7	-7,370
	CCl <sub>4</sub>	-7,940	0.4	-8,036
$I_2 + Br_2 \rightleftharpoons 2IBr$	Gas	-2,744	3.1	-3,443
	CCl <sub>4</sub>	-3,260	1.1	-3,355
$Br_2 + Cl_2 \rightleftharpoons 2BrCl$	Gas	-600	2.25	-1,257
	CCl <sub>4</sub>	-756	-0.1	-714

The state of reference for the gaseous reactions is the ideal gas state at a pressure of one atmosphere, and for the reactions in solutions is the hypothetical solution in which each solute in turn is present at unit mole fraction. In our notation, therefore, we denote the values given in column 3 as  $\Delta H_g^\circ$  and  $\Delta H_m^\circ$  respectively (equation (54)). The equilibrium constant, obtained by using equation (26), is found to be but slightly affected by the solvent, as is to be expected in view of the similarity of the reactants and resultants, and of the stoichiometric symmetry of the reactions.

† *J. Amer. Chem. Soc.*, **55**, 4489, (1933).

*The van 't Hoff-Dimroth Relation*

The first attempt to relate the velocity of reaction in solution to the solubility is due to van 't Hoff,<sup>†</sup> whose ideas were put to the test by Dimroth.<sup>‡</sup> Let us suppose the reversible reaction



to reach equilibrium in the gaseous phase. Then

$$K_g = \frac{p_B}{p_A}. \quad (61)$$

The same value of  $K_g$  is, of course, found if concentrations, rather than the partial pressures, are used. In solution, at the same temperature and pressure, we have

$$K_c = \frac{c_B}{c_A}. \quad (62)$$

But, by Henry's law, of which equation (40) is a variant, we can relate the two equilibrium constants, and obtain

$$K_g = \frac{c_B/s_B}{c_A/s_A} = K_c \left( \frac{s_A}{s_B} \right). \quad (63)$$

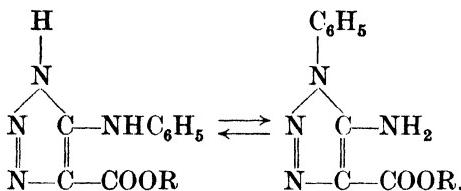
If, therefore, the concentrations of the solutes in any solvent be expressed as fractions of their solubilities, the resulting equilibrium constant should be independent of the solvent, and numerically equal to the constant for the gaseous reaction. The argument holds for a liquid or solid solute. By measuring the equilibrium concentrations and the solubilities of the isomeric forms of the methyl and ethyl esters of 1-phenyl-5-aminotriazole carboxylic acid in various solvents, Dimroth found  $K$  to be sensibly independent of the solvent (Table 13).

Table 13

Solvent	Methyl ester			Ethyl ester		
	$c_B/c_A$	$s_B/s_A$	$\frac{c_B/s_B}{c_A/s_A}$	$c_B/c_A$	$s_B/s_A$	$\frac{c_B/s_B}{c_A/s_A}$
$(C_2H_5)_2O$	21.7	53.0	0.40	20.7	8.4	2.4
$C_2H_5OH$	2.3	7.0	0.33	4.56	2.1	2.3
$C_6H_5CH_3$	1.8	4.3	0.33	1.53	0.74	2.1
$C_6H_6$	1.02	3.2	0.32	1.20	0.60	2.4
$C_6H_5NO_2$	0.80	2.2	0.36	0.85	0.33	2.6
$CHCl_3$	0.32	1.1	0.32	0.32	0.19	1.7

<sup>†</sup> *Lectures on Theoretical and Physical Chemistry*, 1, 221, (1898).

<sup>‡</sup> *Annalen*, 377, 127, (1910).



The van 't Hoff-Dimroth relation has been shown to hold also for the equilibria between the tautomeric forms of benzoyl camphor† and of ethyl acetoacetate.‡ The relative velocities of the two opposing reactions for either of the equilibria in Table 13 varies about sixty-fold when ordinary concentrations are employed. A value of  $K$  much nearer unity results with the use of the corrected concentrations. This in itself strengthens the case, for we have seen that the ratio of the velocity coefficients for opposing isomeric changes must be of this order of magnitude.

Now let us combine the kinetic expression (equation (4)) for an equilibrium of this type with equation (63). We obtain

$$K_g = \frac{k_A s_A}{k_B s_B}. \quad (64)$$

Since  $K_g$  is a function of the reaction only, it is of interest to inquire whether the terms  $(k_A s_A)$  and  $(k_B s_B)$  separately may also be independent of the medium. There is no reason why this should be so, but Dimroth§ found that the velocity of conversion of the enol form of the ethyl ester of 1-phenyl-5-hydroxytriazole carboxylic acid into the keto form is in fact nearly inversely proportional to the solubility of the enol in a number of solvents. To a certain extent, however, the agreement suggested by the figures in column 4 (Table 14) is illusory.

Table 14

Solvent	$k_A$ at 10° C. (minutes <sup>-1</sup> )	$s_A$ at 10° C. (grams/litre)	$k_A s_A$	$\frac{k_A s_A}{(s_A \text{ in molar fractions})}$
CH <sub>3</sub> OH	0.00053	218.0	0.116	4.67
C <sub>2</sub> H <sub>5</sub> OH	0.00103	97.7	0.101	5.85
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	0.00110	90.0	0.099	9.12
(CH <sub>3</sub> ) <sub>2</sub> CO	0.00527	56.5	0.298	21.7
CHCl <sub>3</sub>	6.0211	8.8	0.186	14.8
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	0.0267	12.0	0.320	32.7
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.0460	6.5	0.299	31.3
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.0550	3.2	0.176	14.4

† Dimroth and Mason, *Annalen*, **399**, 91, (1913).

‡ Meyer, *ibid.*, **380**, 231, (1911).

§ Loc. cit.

The proper value of  $s$  to use is not the absolute solubility but the ratio of the solubility in the various solvents to the standard solubility in some reference state (cf. equation (40)). Dimroth's data have accordingly been corrected by multiplying  $k_A s_A$  by the molecular volume of the pure solvents. This has the effect of diminishing an already rather doubtful regularity. The position may therefore be summed up by stating that the velocity coefficient ( $k_A$ ) measured in the usual way varies about one-hundredfold in the different solvents, but when the solubility correction is introduced the factor reduces to 7.

If  $k_A s_A$  were found to be independent of the medium, the sum ( $E_A + q_A$ ) should also have a value characteristic of the reaction only, where  $q_A$  is the molecular heat absorbed during dissolution. Freundlich and Richards's results† on the velocity of cyclization of  $\epsilon$ -chloroamylamine into piperidine hydrochloride indicate that this condition is approximately fulfilled. In aqueous solution  $E_A = 20,670$  calories and  $q_A = 450$ ; hence  $E = 21,120$ . The corresponding values in tetrachlorethane as solvent are 14,420 and 5,200, giving  $E = 19,620$ . The organic solvent was not dry, so that the latter figure is probably too low. Within the limits of error the sum of the observed critical increment and the heat of solution is independent of the solvent in this particular case.

The lack of constancy in the product  $k_A s_A$  is still more marked in the case of a reaction such as the decomposition of nitrogen pentoxide (Table 15),‡ which is not opposed by another unimolecular process. It is worthy of note that, in so far as one is able to compute, the product  $k_A N_A$ , where  $N$  is the molar fraction in the three phases, is reasonably constant, as would be expected if the equilibrium constant,  $K_m$ , were resolvable into independent components. The

Table 15  
*The Decomposition of Nitrogen Pentoxide in Various Media*

	$s_A$ Saturation concentration (gram molecules/litre)	$-\frac{dc}{dt} \times 10^6$	$k_A \left( = -\frac{dc}{dt} \frac{1}{c} \right) \times 10^6$ (seconds $^{-1}$ )
Gas phase	0.0102	0.0080	0.79
Nitromethane	4.38	5.92	1.35
Carbon tetrachloride	4.78	8.75	1.83

† *Z. physikal. Chem.*, **79**, 681, (1912).

‡ After Eyring and Daniels, *J. Amer. Chem. Soc.*, **52**, 1472, (1930).

inference is that this reaction would proceed in the liquid state with the same velocity as in the gaseous state at the same temperature.

These experiments were undertaken with a view to deciding whether the instantaneous velocity of reaction,  $-dc/dt$ , is determined by the concentration,  $c$ , or by the activity,  $a$ —a subject about which much has been written. The weight of evidence is on the side of the former view. In chemical kinetics we are less concerned with the temporal variation of a mathematical function, however convenient it may have proved in the formal codification of facts, than in finding how many molecules are formed by a reaction in unit time and in unit volume. That is why the velocity coefficient is always expressed in terms of concentrations. In the nature of the problem, however, there can be no conflict between what thermodynamics has to say on systems where chemical change has come to a stop, and what chemical kinetics has to say on systems where chemical change is in full swing.

### *Equilibria in Aqueous Solution*

Raoult's law is but the alphabet of solutions, necessary as a preliminary approach to the problem, but inadequate for the description of aqueous solutions. When the field of force surrounding a molecule is vastly altered by dissolution we must look for a radically different interpretation of the solvent effect. This is provided by the conception of definite union between solute and solvent molecules.

We may regard the energy of activation,  $E$ , of a chemical reaction as the limiting value of the internal energy which the reacting molecules can accommodate in the gaseous state. If  $E_s$  is the energy of activation in solution, and  $q_s$  the internal energy gained on dissolution, then the relationship

$$E = E_s + q_s \quad (65)$$

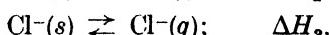
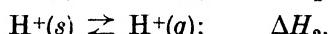
should hold for all media. This equation is the kinetic analogue of equation (54), but is not limited to cases where  $q_s$  must be identified with the heat of condensation. Although  $E$  may be very large, we know that  $q_s$  also can be very large, so that solvents can greatly reduce the energy of activation, and, by making  $E_s$  relatively small, bring to within the reach of measurement at ordinary temperatures the rates of reactions which are immeasurably slow in the gaseous phase. Water is the most effective solvent in this sense, and the alcohols rank next to it. To gain some idea of the magnitudes

involved, let us consider the dissociation of hydrogen chloride in the gaseous phase, expressing  $\Delta H$  in kilocalories per mole:



and compare it with the corresponding ionization in water, for which we have  $\text{HCl}(s) \rightleftharpoons \text{H}^+(s) + \text{Cl}^-(s); \quad \Delta H = -15$ .

By subtracting, we see that, for the three heats of dissolution:



we have

$$\Delta H_2 + \Delta H_3 - \Delta H_1 = 342.$$

From our previous knowledge, we surmise that  $\Delta H_1$  cannot exceed about 3–4 kilocalories per mole. There are various reasons, into a discussion of which we cannot enter here,† for apportionating the remaining heat effect in the approximate ratio of 3 to 1 for the hydrogen and chloride ions. Roughly, then, we have  $\Delta H_3 = 86$  and  $\Delta H_2 = 259$  kilocalories per gram ion. Comparable magnitudes must hold for differences in energies of activation in gaseous and aqueous systems.

### *Ionization in Aqueous Solution*

Apart from a few isolated equilibria of the types shown in Table 16, most of our knowledge of ionic dissociation in aqueous solution refers

*Table 16*  
*Various Equilibria, not involving Acids, in Aqueous Solution*  
( $T = 298.1^\circ\text{K}$ )

Reference	Reaction	$\Delta S^\circ$ (cals./gm. mole-deg.)	$\Delta H^\circ$ (cals./gm. mole)
(1)	$I^- \rightleftharpoons I_2 + I^-$	2.01	4,470
(2)	$Br^- \rightleftharpoons Br_2 + Br^-$	-0.35	1,580
(3)	$I_2 \rightleftharpoons I^- + I^+$ NH <sub>3</sub>	-28.3	-1,960
(4)	$\text{HN:}-\text{C}-\text{N}(\text{CH}_3)-\text{CH}_3-\text{COOH}$ $\rightleftharpoons$ $\text{HN:}-\text{C}-\text{N}(\text{CH}_3)-\text{CH}_3-\text{CO}$ $\text{H}_2\text{O}$	15.4	4,950
(5)	$[\text{Cr}(\text{H}_2\text{O})_6\text{CNS}]^{4+} + \text{H}_2\text{O} \rightleftharpoons [\text{Cr}(\text{H}_2\text{O})_5]^{\text{+++}} + \text{CNS}^-$	-10.8	190
(6)	$\text{C}_6\text{H}_5\text{OH} + \text{HCl} \rightleftharpoons \text{C}_6\text{H}_5\text{Cl} + \text{H}_2\text{O}$	24.0	9,800

(1) Jones and Kaplan, *J. Amer. Chem. Soc.*, **50**, 1845, (1928).

(2) Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, **28**, 101, (1932).

(3) Winther, *Z. physikal. Chem.*, **B**, **3**, 290, (1929).

(4) Edgar and Shiver, *J. Amer. Chem. Soc.*, **47**, 1170, (1925).

(5) Bjerrum, *Z. anorg. Chem.*, **118**, 131, (1921).

(6) Kilpi, *Z. physikal. Chem.*, **86**, 427, (1914).

† Fajans and Schwartz, *Z. physikal. Chem., Bodenstein Festband*, 717, (1931); Latimer, Pitzer, and Slansky, *J. Chem. Physics*, **7**, 108, (1939)

to the ionization of bases and acids, with the second of which we are now to deal.

Most of the early data obtained electrometrically and conductimetrically on the ionization constants of acids have been presented in empirical formulae showing the relation between  $K$  and various powers of  $t$  (° Centigrade) or of  $(t - 25)$ . While such formulae suffice to summarize the data accurately, especially when  $K$  passes through a maximum or a minimum in the range of investigation, they are clearly not directly amenable to theoretical interpretation. This point was appreciated independently and simultaneously by Pitzer† and Moelwyn-Hughes,‡ who, for very different reasons, examined the literature and recast some of the most reliable data into the form

$$\ln K = I + \left( \frac{\Delta C_P}{R} \right) \ln T - \frac{\Delta H_0^{\circ}}{RT} \quad (66)$$

as suggested by Harned, MacInnes, and their collaborators.§ As these are independent calculations, sometimes from different sets of data, they are reproduced fully in Tables 17 and 18, omitting only

*Table 17*  
*Thermodynamic Constants for the Ionization of Weak Acids in Aqueous Solution at 25°*

Acid	$\Delta H^{\circ}$ , cals./mole	$\Delta F^{\circ}$ , cals./mole	$-\Delta S^{\circ}$ , cals./deg.-mole	$-\Delta C_P^{\circ}$ , cals./deg.-mole
Acetic	-112	6,488	22.1	34
Metaboric	3,360	12,599	31.0	43
Butyric	-691	6,574	24.4	46
Carbonic (first)	1,843	8,683	22.9	—
Chloroacetic	-1,170	3,900	17.0	35
Chlorous	-4,100	2,670	22.7	—
Formic	-13	5,120	17.2	41
Hypochlorous	3,320	10,100	22.8	—
Phosphoric (first)	-1,880	2,898	16.0	—
Propionic	-168	6,650	22.9	38
Sulphurous (first)	4,000	2,725	22.6	—
Water	13,358	19,093	19.24 (27)	50
Carbonic (second)	3,500	13,983	35.2	—
Phosphoric (second)	800	9,830	30.3	—
Sulphuric (second)	-5,200	2,620	26.3	—
Phosphoric (third)	3,500	16,300	43	—

† *J. Amer. Chem. Soc.*, **59**, 2365, (1937).

‡ *Trans. Faraday Soc.*, **34**, 91, (1938).

§ Harned and Embree, *J. Amer. Chem. Soc.*, **56**, 1042, (1934); Harned and Ehlers, *ibid.*, **55**, 2379, (1933); **54**, 1350, (1932); B. B. Owen, *ibid.*, **56**, 24, (1934); D. D. Wright, *ibid.*, **56**, 314, (1934); W. J. Hamer, *ibid.*, **56**, 8, 860, (1934); MacInnes, *The Principles of Electrochemistry*, Reinhold, New York, (1939).

the references to original sources. In Pitzer's Table (17) the terms in brackets refer to the first and second dissociation constants. Pitzer points out that, although the changes in heat content and in standard free energies vary widely,  $\Delta S^0$  and  $\Delta C_P$  are always negative, and, for first ionizations, have roughly the values -22 and -40

*Table 18*  
*Ionization Constants in Water at 25° C. and 1 Atmosphere Pressure*

Electrolyte	$K$ , molality or moles/litre	$\Delta H$ , cals./mole	$\Delta C_P$ , cals./mole-degree
D <sub>2</sub> O	$3.524 \times 10^{-17}$	+ 13,420	- 42.8
H <sub>2</sub> O	$1.805 \times 10^{-16}$	13,450	- 42.8
H <sub>2</sub> O	$1.819 \times 10^{-16}$	13,481	- 42.5
H <sub>2</sub> CO <sub>3</sub> (first)	$4.31 \times 10^{-7}$	2,075	- 82
H <sub>2</sub> . COOH	$1.772 \times 10^{-4}$	- 13	- 40.9
CH <sub>3</sub> . COOH	$1.754 \times 10^{-5}$	- 112	- 33.9
C <sub>2</sub> H <sub>5</sub> . COOH	$1.336 \times 10^{-5}$	- 168	- 37.7
nC <sub>8</sub> H <sub>7</sub> . COOH	$1.515 \times 10^{-5}$	- 691	- 46
NH <sub>4</sub> OH	$1.81 \times 10^{-5}$	+ 790	- 52.5
I <sub>2</sub>	$1.84 \times 10^{-5}$	- 1,964	—
Violuric acid	$2.73 \times 10^{-6}$	+ 3,650	- 38.2
NH <sub>2</sub> . CH <sub>2</sub> . COOH (basic)	$6.04 \times 10^{-5}$	+ 2,765	- 22.2
HO. CH <sub>2</sub> . COOH	$1.48 \times 10^{-4}$	+ 210	- 39.2
Cl. CH <sub>2</sub> . COOH	$1.378 \times 10^{-3}$	- 1,170	- 34.9
NH <sub>2</sub> . CH <sub>2</sub> . COOH (acidic)	$4.47 \times 10^{-3}$	+ 1,159	- 30.6
H <sub>2</sub> PO <sub>4</sub> (first)	$7.52 \times 10^{-3}$	- 1.764	- 42.8
H <sub>2</sub> SO <sub>4</sub> (first)	$1.30 \times 10^{-2}$	- 3,860	—
HCl	$2.50 \times 10^{+7}$	- 17,900	—

calories/gram mole-degree. He is able also to offer a semi-quantitative interpretation of these facts in terms of Latimer's theory,† to which the reader is referred for an account of the most accurate information on entropies of ions. It is worth observing, in continuation of Pitzer's discussion, that, although the standard entropy changes for most of the primary ionizations lead to a common value of about -20, a higher and equally uniform value is found for the formation of two ions of the complete octet structure. Thus, for example, in the ionization of H<sub>2</sub>O, D<sub>2</sub>O, I<sub>2</sub>, and HCl, the values of  $-\Delta S^0$  are, respectively, -26.82, -26.80, -28.3, and -26.2. This distinction is visible in Fig. 1, in which the full line has the theoretical slope of  $-(2.303R)^{-1}$ , which the results would lead us to expect for series of equilibria with a constant difference in standard entropies.

† Latimer, *Chem. Rev.*, **18**, 349, (1936); Latimer, Schutz, and Hicks, *J. Chem. Physics*, **2**, 82, (1934).

The average value of  $-\Delta C_P$  from Table 18, after omitting some obviously high cases, is  $-38.8$ . That this is a fairly representative figure may be seen from some further, but much earlier data taken from the 1912 edition of Landolt-Börnstein's *Tabellen* (see Table 19).

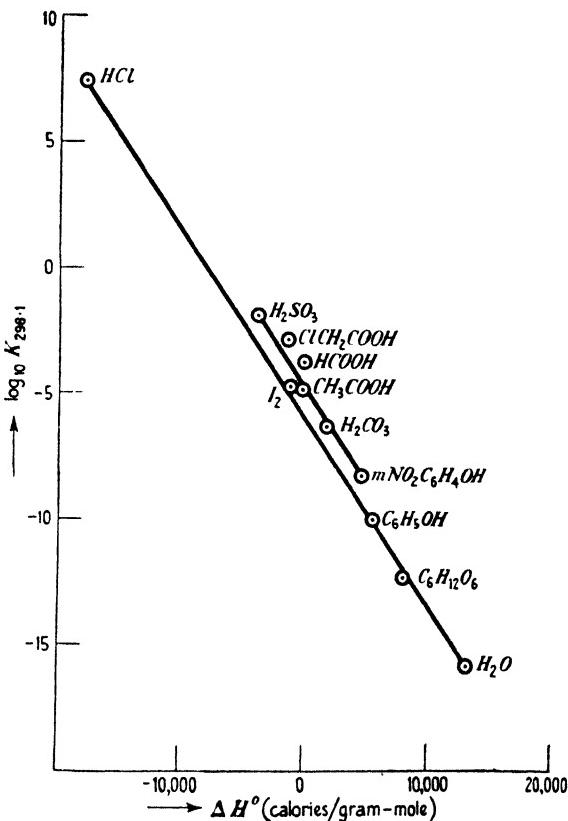


FIG. 1. Ionization constants and heats of ionization in water.

If we accept the specificity in the values of  $\Delta C_P$  we arrive at reasonable values of  $\Delta H^\circ_0$ , the heat effect which would attend the ionization in water supercooled to the absolute zero of temperature (column 4). The drawback to such an acceptance, however, is that the values of  $I$  in equation (66) then vary inordinately from one reaction to another.<sup>†</sup> Pitzer's suggestion of an approximate constancy in  $\Delta C_P$  may therefore be accepted. Taking it to be  $-36$  for all the acids

<sup>†</sup> This equation means that  $\partial^2 \Delta C_P / \partial T^2$  is zero. The observed values are always small, and seldom exceed  $-0.23$ , which is occasionally less than the errors in experiment.

considered, we compute the figures given in the last column of Table 19. Some of these have been inserted in Fig. 1.

Table 19

*Ionization Constants ( $K = [H^+][A^-]/[HA]$ ) and Heats of Ionization in Water at 25° C.*

Acid	$K$	$\Delta C_P$ (calories/gm. mole-degree)	$\Delta H_0^\circ$ (from complete data)	$\Delta H_0^\circ$ (assuming $\Delta C_P = -36$ in all cases)
d-Glucose	$5 \cdot 10 \times 10^{-13}$	-40	20,030	18,840
C <sub>6</sub> H <sub>5</sub> OH	$1 \cdot 09 \times 10^{-10}$	-43.5	18,975	16,520
p-NO <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> OH	$6 \cdot 75 \times 10^{-8}$	-21	11,105	15,468
m-NO <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> OH	$5 \cdot 30 \times 10^{-9}$	-47.9	19,260	15,473
CH <sub>3</sub> .COOH	$1 \cdot 83 \times 10^{-5}$	-38.9	11,500	10,475
C <sub>6</sub> H <sub>5</sub> .COOH	$1 \cdot 40 \times 10^{-5}$	-46.0	13,610	10,625
o-NH <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> OH	$1 \cdot 06 \times 10^{-5}$	-38.1	14,625	13,985
p-CH <sub>3</sub> O.C <sub>6</sub> H <sub>4</sub> OH	$3 \cdot 20 \times 10^{-5}$	-36.3	11,025	10,950
C <sub>6</sub> H <sub>5</sub> .COOH	$6 \cdot 52 \times 10^{-5}$	-42	12,690	10,860
o-ClC <sub>6</sub> H <sub>5</sub> .COOH	$1 \cdot 32 \times 10^{-3}$	-36	8,475	8,475
o-IC <sub>6</sub> H <sub>5</sub> .COOH	$1 \cdot 40 \times 10^{-3}$	-23	4,190	8,350
m-IC <sub>6</sub> H <sub>5</sub> .COOH	$1 \cdot 60 \times 10^{-4}$	-35.9	13,370	14,020
m-NO <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> .COOH	$3 \cdot 53 \times 10^{-4}$	-38	12,730	11,121
o-NO <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> .COOH	$6 \cdot 35 \times 10^{-3}$	-29	5,465	8,660
m-HO.C <sub>6</sub> H <sub>5</sub> .COOH	$8 \cdot 33 \times 10^{-5}$	-26	7,870	10,850
o-HO.C <sub>6</sub> H <sub>5</sub> .COOH	$1 \cdot 06 \times 10^{-3}$	-44	14,180	11,755
o-CH <sub>3</sub> .C <sub>6</sub> H <sub>5</sub> .COOH	$1 \cdot 25 \times 10^{-4}$	-30	7,635	9,460
m-CH <sub>3</sub> .C <sub>6</sub> H <sub>5</sub> .COOH	$5 \cdot 60 \times 10^{-5}$	-36	10,965	10,965
p-CH <sub>3</sub> .C <sub>6</sub> H <sub>5</sub> .COOH	$4 \cdot 30 \times 10^{-5}$	-32	9,730	11,005
C <sub>6</sub> H <sub>5</sub> .CH:CH.COOH	$3 \cdot 68 \times 10^{-5}$	-31	9,770	11,370
C <sub>6</sub> H <sub>5</sub> .CH:CBr.COOH	$1 \cdot 22 \times 10^{-2}$	-28	5,070	7,625

It will be clear from the forms of equations (25) and (66) that  $\Delta C_P$  for the equilibrated system is the difference between the temperature coefficients of the Arrhenius energies of activation of the two reactions. We have already seen that  $-dE_2/dT$  for bimolecular ionic reactions is a small quantity (equation IV (21)). We have also seen (p. 60) that  $-dE_1/dT$  for unimolecular reactions in water is often within the region 20 to 60 calories/gram mole-degree. Thus the principal difference in mechanism between the ionization of an acid in water and a simple hydrolysis such as that of the methyl halides is that only the former is successfully opposed by a reverse reaction between the ions formed.

Concerning the accuracy with which  $\Delta C_P$  can be measured electro-metrically, we note from Table 18 that two sets of independent data have yielded results agreeing to within  $\pm 0.15$  calories/gram mole-degree. Such excellent agreement may, however, be illusory. In the

case of the ionization of water, another and somewhat more accurate method is available for determining this quantity, i.e. by algebraic addition of the partial molar heats, which can be measured independently for solutions of electrolytes.<sup>†</sup> By applying it to the ionization of water, we have, following Pitzer<sup>‡</sup>

$$\begin{aligned}\Delta C_P &= C_P(\text{H}^+) + C_P(\text{OH}^-) - C_P(\text{H}_2\text{O}) \\ &= -15.9 - 16.1 - 18.0 = -50.\end{aligned}$$

That an error of some 8 calories/gram mole-degree may occur in electrometric measurements should not be overlooked when we determine  $dE_A/dT$  by the more difficult methods of chemical kinetics.

We now inquire into the order of magnitude which may, on kinetic considerations, be expected for the ionization constant,  $K$ , of a monobasic<sup>§</sup> acid, ionizing according to the familiar scheme



in aqueous solution at atmospheric pressure and at 25° C. The kinetic expression for the equilibrium constant at great dilution is

$$K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{k_1}{k_2}. \quad (67)$$

We shall regard the dissociation of the acid as unimolecular and the union of the ions as bimolecular.

An application of equation IX (5) and of the formula developed in Chapter IV for the velocity coefficient of a bimolecular ionic reaction between ions of various valencies leads to the equation

$$\ln K = \ln \left\{ \frac{500\eta}{rM_{\text{HA}}} \left( \frac{9\pi M_{\text{H}^+}}{8RT} \right)^{\frac{1}{2}} \right\} - \left( \frac{E_1 - E_2}{RT} \right) + \frac{z_A z_B \epsilon^2}{DrkT} (1 - \kappa r) \quad (68)$$

in which  $M$  is the molecular weight (oxygen = 16). For an acid of molecular weight 60 grams, with a critical separation of 3 Å and a value of 10,000 calories for  $(E_1 - E_2)$ , we thus anticipate  $K$  in water at 298.1° K. to have the order of magnitude of  $10^{-7}$  litres/gm. mole.

Suppose that we are primarily interested in the effect of ionic

<sup>†</sup> Randall and Rossini, *J. Amer. Chem. Soc.*, **51**, 323, (1929); Gucker, *Chem. Rev.*, **13**, 111, (1933).

<sup>‡</sup> *Loc. cit.*

<sup>§</sup> For a treatment of the ionization of dibasic acids, see Ingold, *Trans. Chem. Soc.*, **2179**, (1931); I. Jones and F. G. Soper, *ibid.*, **133**, (1936).

environment on the equilibrium constant, while all the other variables are kept constant; we can then clearly write

$$\ln K = \text{a constant} - \frac{z_A z_B \epsilon^2 \kappa}{DkT}. \quad (69)$$

The effect of ionic strength on the dissociation constant thus follows the Bjerrum-Brönsted relationship,† but, because  $k_2$  appears in the denominator of the kinetic expression for  $K$ , the sign of the electrolyte

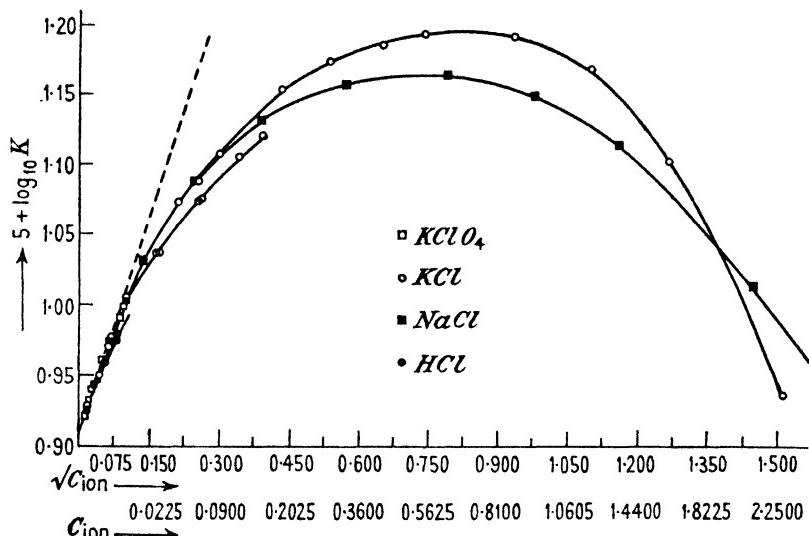


FIG. 2. The influence of electrolytes on the dissociation of dinitrophenol.

effect is reversed. Only in very dilute solution is this equation obeyed. The deviation at a concentration of 1/100 molar is 3·5 per cent., and becomes greater as the concentration increases. These facts are illustrated in Fig. 2, which refers to the dissociation of  $\alpha$ -dinitrophenol in the presence of various electrolytes in aqueous solution at 25° C.‡

Let us next examine the form taken by equation (68) for results extrapolated to zero ionic strength ( $\kappa = 0$ ). The ionization constant in an infinitely dilute solution can now be written in the form

$$\ln K = \ln K^0 + \frac{z_A z_B \epsilon^2}{DrkT}. \quad (70)$$

† Bjerrum and Larsson, *Z. physikal. Chem.*, **127**, 358, (1927); Brönsted, *Chem. Rev.*, **5**, 231, (1928).

‡ von Halban and Kortüm, *Z. physikal. Chem.*, **A**, **170**, 351, (1934), who find  $K = 8.13 \times 10^{-5}$  at this temperature, and  $\Delta H^0 = 2,950 \pm 70$  calories per mole.

The term  $K^0$  is a function of the temperature and other variables about which our knowledge is meagre. Let us suppose that we wish to discern the effect of changing the dielectric constant of the medium

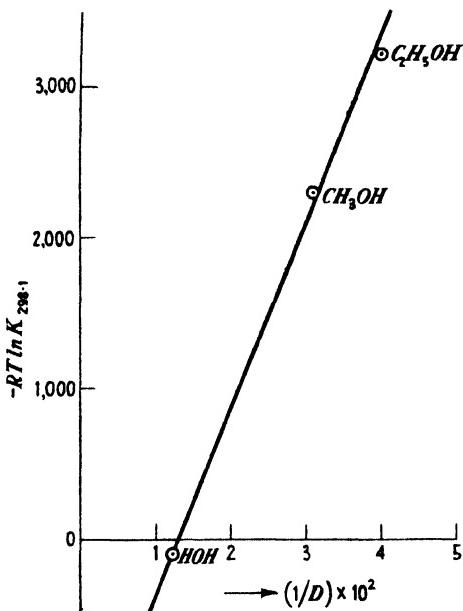


FIG. 3. The ionization of silver nitrate in various solvents.

while keeping all the other variables constant. We have, by differentiation,

$$\left[ \frac{d \ln K}{d(1/D)} \right]_{T,P} = \frac{z_A z_B \epsilon^2}{r k T}, \quad (71)$$

as was first shown by Wynne-Jones.<sup>†</sup> Let us apply this relation to the results obtained by C. W. Davies<sup>‡</sup> in the case of silver nitrate.

Table 20  
The Ionization of  $\text{AgNO}_3$  in Various Solvents at  $25^\circ\text{C}$ .

Solvent	$K$	$\Delta G^0 = -RT \ln K$
HOH	$1.17 \times 10^0$	-95
$\text{CH}_3\text{OH}$	$2.05 \times 10^{-2}$	+2,297
$\text{C}_2\text{H}_5\text{OH}$	$4.42 \times 10^{-3}$	+3,210

His data are given in Table 20; and in Fig. 3,  $\Delta G^0$  is plotted as a function of  $1/D$ . From the gradient of the curve, we find that

<sup>†</sup> Proc. Roy. Soc., A, 140, 440, (1933).

<sup>‡</sup> The Conductivity of Solutions, 2nd ed., Chapman and Hall, London, (1934).

$r = 2.681 \text{ \AA}$ . This figure compares excellently with the sum of the radii determined from ionic mobilities, which is  $1.43 + 1.245 = 2.675 \text{ \AA}$ , a value independent of the solvent. It is interesting and important to find such close agreement between these results and those furnished by kinetic experiments (Chapter IV).

Finally, we differentiate equation (68) with respect to the temperature, obtaining for the heat of ionization and for the change in specific heat

$$\Delta H = (E_1 - E_2 - \frac{1}{2}RT) - B(T) + \frac{N_0 z_A z_B \epsilon^2}{Dr} (LT - 1), \quad (72)$$

$$\text{and } \Delta C_P = \frac{d(E_1 - E_2 - \frac{1}{2}RT)}{dT} - \left( \frac{dB}{dT} \right)_P + \frac{N_0 z_A z_B \epsilon^2 L^2 T}{Dr}. \quad (73)$$

### *The Decrease in Specific Heat attending Ionization in Water at 298.1°K.*

We see from equations (72) and (73) that the two thermal quantities with which we are concerned may be resolved into three components. The first is that due to the intrinsic heat change, which, as we shall see, is largely due to the change of certain oscillatory motions from weak ones, obeying classical laws, to firm ones, obeying quantal laws. The second term arises from the variation of the frequency of dissociation with respect to temperature, and is the term about which we know least. The last term is the electrostatic contribution to the change in specific heat at infinite dilution (equation IV (21)).

Since these formulae were derived† there have been many efforts to intensify the inquiry into the nature of the three contributions

$\Delta C_P = \Delta C_P(\text{vibrational}) + \Delta C_P(\text{collisional}) + \Delta C_P(\text{electrostatic})$ , but it is only with a few of them that we shall here be able to deal. Our problem is to explain a total diminution in the specific heat of ionizations in water at 25° C., which amounts to anything from 36 to 50 calories per gram-mole-degree. Let us take  $\Delta C_P$  to have a target value of  $-43 \pm 7$ .

We shall first consider the electrostatic contribution for a univalent electrolyte, which, according to equation (73) is seen to be

$$\Delta C_P = -\frac{N_0 \epsilon^2 L^2 T}{Dr}. \quad (74)$$

There has been much difference of opinion as to the correct values of

† *Trans. Faraday Soc.*, 34, 91, (1938).

$r$  to use in this expression. It is clear that the whole effect could be shouldered on to the electrostatic term if once we are prepared to accept a value of the critical interionic distance as low as  $0.7 \pm 0.3 \text{ \AA}$ . Such a view is taken by La Mer† and by Baughan,‡ whose treatment is distinguished from the earlier one§ by the substitution of  $\frac{1}{2}(1/r_1 + 1/r_2)$  for  $1/r_{1,2}$  in all the formulae. This extreme view of the problem, however, is not one that can be sustained; and although the original computations made use of a somewhat conservative estimate of  $3 \text{ \AA}$ ., there can be no doubt, in the light of the experiments described in Chapter IV, that this value is much nearer the mark. We are still in the dark about the precise value of  $r$ , but consider that the weight of evidence is strongly against its being lower than  $2 \text{ \AA}$ ., and points to a value in the neighbourhood of  $2.5 \text{ \AA}$ . as the most probable one. This estimate, with which there will be no general agreement, leads us to the conclusion that the maximum that can be expected from the electrostatic contribution to the decrease in the specific heat is 10.5 calories/gram mole-degree. It is to be observed that this estimate, based on equation (74), is considerably higher than that found by the Born method of charging the two ions.|| We are now left with a quantity  $-32.5 \pm 7$  to be explained in terms of the other contributions.

Pitzer†† has shown that the change in the nature of the vibrational motion of water molecules on entering the fields of the ions can explain the order of magnitude of the observed  $-\Delta C_P$ , but he is inclined to attribute the overwhelming if not complete effect to this cause. The idea is equivalent to one contemporaneously made that the energy of activation of the dissociation is distributed among a number of classical oscillators. Pitzer's argument may be stated somewhat as follows. In order to explain the specific heat of water it may be assumed that all the nine motions of which its atoms are capable are weak oscillations, although this supposition is inconsistent with the spectra of liquid water. Each vibration contributes  $R$  to the specific heat, which is then 18 calories per gram mole. In the field of the ion, the three internal vibrations may be regarded as unaffected, and the remaining ones as having been converted to a spinning of the hydrogen atoms about an axis passing from the centre of the ion through

† *J. Amer. Chem. Soc.*, **62**, 617, (1940).

‡ *J. Chem. Physics*, **7**, 951, (1939).

§ *Trans. Faraday Soc.*, **34**, 91, (1938).

|| Everett and Coulson, *Trans. Faraday Soc.*, **36**, 633, (1940).

†† *Loc. cit.*

the centre of the water molecule and to a translation along the radial line. The specific heat of the attracted water molecule would then be about one-half of its value in water, corresponding to a loss of 9 calories for each molecule attached to an ion. The smallest coordination number envisaged is 4 for each ion; hence the value of  $-\Delta C_P$  (vibrational) is about -72 calories/degree. On this basis, we are left with  $\Delta C_P$ (collisional) of  $+40 \pm 7$ . According to the present treatment,  $\Delta C_P$ (collisional) is  $-(dB/dT)_P$ , which, at  $25^\circ$  C. is 30 calories/gram mole-degree. Summarizing, we have

$$\begin{aligned}\Delta C_P &= \Delta C_P(\text{vibrational}) + \Delta C_P(\text{collisional}) + \Delta C_P(\text{electrostatic}) \\ &= \quad\quad\quad -72 \quad\quad\quad +30 \quad\quad\quad -10.\end{aligned}$$

The most suspect of these values is the second, which arises, not from the magnitude of the solute-solvent vibration frequency, but from the curious manner in which it varies with temperature. In the treatment given here, we have assumed that this frequency is reproduced by the simple equation  $Z = 3\pi\eta\sigma/2m$ , where  $\eta$  is the viscosity of the solvent, rather than by the relaxation frequency suggested in the earlier treatment. Although the assumption places an additional burden on the vibrational and electrostatic contributions, it is not a greater one than they can carry.

Everett and Coulson† have considered in greater detail the motions of the water molecules in the fields of the ions, and conclude that they cannot account for a total  $\Delta C_P$  of more than -32 unless radii of less than 1 Å. are allowed.

In conclusion, it can be said of the kinetic treatment of equilibria in solution, that despite its shortcomings it has stimulated work in, and cast considerable light upon, a problem which, from the purely thermodynamic angle, has long remained obscure.

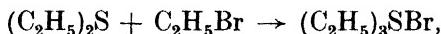
† *Loc. cit.*

## VII

### REACTIONS BETWEEN POLAR MOLECULES

THERE are relatively few reactions between undissociated molecules in solution. The reason is that solvents of high dielectric capacity are the commoner and more useful ones; in these, most solutes ionize, and an easier means of chemical change is thereby provided. Our knowledge of reactions between molecules in solution chiefly arises, therefore, from the comparatively small amount of work which has been done in non-ionizing media such as hexane, benzene, and carbon tetrachloride. Limitations are frequently imposed by the narrow temperature range in which these solvents normally exist, by the limited solubility of many reactants in them, and by the catalytic effect of impurities—difficult to remove entirely—of which water and oxygen are the worst offenders.

Of those bimolecular reactions with rates proportional to the concentration of both reactants, only a small proportion have velocities in agreement with the predictions of the collision theory. The combination of diethyl sulphide with ethyl bromide,

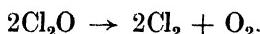


in benzyl alcohol solution would appear to afford an excellent example (see Table 1 of Chapter III). The bimolecular coefficients have not been, however, obtained directly, but, as described in Chapter VI, from the unimolecular velocity of decomposition of the sulphonium salt and the equilibrium constant. The agreement may thus be illusory, and, in fact, a direct study of the kindred reaction,



in acetone and in ethyl alcohol solutions† indicates values of  $P$  as low as  $10^{-2}$  to  $10^{-4}$ , according to the type of collision formula adopted. Kinetically, the formation of sulphonium salts would thus appear to fall in line with the formation of ammonium salts.

The decomposition of chlorine monoxide,



has been investigated in the gaseous phase and in certain inert solvents (p. 239), but it does not proceed by an uncomplicated

† Syrkin and Gladishev, *Acta Physicochim. U.S.S.R.*, **2**, 291, (1935).

bimolecular mechanism. The replacement by iodine of the nitrogen in diazoacetic ester,



has been found to be a bimolecular reaction in carbon tetrachloride solution, having velocity coefficients which are reproduced by the equation

$$k = 2 \cdot 21 \times 10^{11} \times e^{-20230/RT}. \dagger$$

In this case; also, the exact role of subsequent reactions cannot be accurately assessed. Their utmost influence could reduce the value of  $P$  from unity, which appears to be the probable value, to about 1/50, which is nevertheless a possible one. It is not to be concluded that no bimolecular reaction has yet been found in carbon tetrachloride solution to proceed with the velocity predicted by the simple theory. When we come to discuss catalysed unimolecular reactions in this solvent we shall find a number of cases showing excellent agreement. They include the decomposition of ethylene di-iodide catalysed by iodine atoms, and various instances of mutarotations and of the Beckmann transformation, catalysed by a variety of polar molecules.

There are numerous reactions in aqueous solution and in hydroxylic media generally which ostensibly belong to the category of reactions between un-ionized polar molecules. The pseudo-unimolecular constants‡ for the hydrolysis of a number of substituted benzyl chloride in 50 per cent. aqueous alcoholic solution at 30 and 83° C. have been shown§ to be reproducible within the accuracy of the experiments by the equation

$$k = \frac{3\pi\eta\sigma}{2m} e^{-E/RT}. \quad (1)$$

The difference of 200 between the rates of the fastest and slowest of the reactions listed in Table 1 is seen to be due almost entirely to changes in the energy of activation. This agreement, however, does not prove that the reaction takes place between uncharged particles: ions are always present, and may play a part. This suspicion is strengthened by the fact that more than one molecule of water is generally needed to hydrolyse one molecule of ester. Esters which hydrolyse easily in liquid water can be distilled in steam without

† Newling, Staveley, and Moelwyn-Hughes, *Trans. Faraday Soc.*, **29**, 1155, (1933).

‡ Olivier, *Rec. trav. chim. Pays-bas*, **42**, 775, (1923); **56**, 247, (1937).

§ *The Kinetics of Reactions in Solution*, 1st ed., p. 161, (1933).

suffering decomposition. Provided, however, that a continuous medium surrounds the two reactants, there is no reason to doubt that reactions of the kind under consideration can take place between un-ionized molecules. The necessity for a continuous molecular environment is a paramount one, and explains why the investigation of reactions between molecules cannot be separated from an investigation of the solvent effects.

Table I

*The Hydrolysis of Substituted Benzyl Chlorides in 50:50 Water-Ethyl Alcohol (E of equation (1) has been taken as  $E_A + 3,425$  calories in each case)*

Reactant	$E_A$	$\sigma \times 10^8$ (eq. I(17))	$k_{30^\circ} \times 10^7$ (secs. <sup>-1</sup> )		$\frac{k_{\text{calc}}}{k_{\text{obs}}}$
			Obs.	Calc.	
C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> Cl	19,900	5.3	18.5	125	6.8
<i>o</i> -CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> .CH <sub>2</sub> Cl	19,790	5.5	91.7	140	1.5
<i>m</i> -,"	20,190	5.5	24.0	73.6	3.1
<i>p</i> -,"	20,390	5.5	173	52.0	0.4
<i>o</i> -NO <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> .CH <sub>2</sub> Cl	22,250	6.3	0.867	2.18	2.5
<i>m</i> -,"	21,780	6.3	1.05	4.76	4.5
<i>p</i> -,"	21,990	6.3	0.818	3.37	4.1
<i>m</i> -CO <sub>2</sub> H.C <sub>6</sub> H <sub>4</sub> .CH <sub>2</sub> Cl	21,350	5.7	3.15	8.89	2.8
<i>p</i> -,"	21,560	5.7	2.02	6.29	3.1
<i>o</i> -Br.C <sub>6</sub> H <sub>4</sub> .CH <sub>2</sub> Cl	21,110	6.5	3.93	12.7	3.2
<i>m</i> -,"	21,870	6.5	2.45	3.58	1.5
<i>p</i> -,"	21,550	6.5	7.62	6.08	0.8
2:6-Br <sub>2</sub> C <sub>6</sub> H <sub>4</sub> .CH <sub>2</sub> Cl	22,460	7.0	1.19	1.04	0.9
2:4-	22,490	7.0	1.82	0.99	0.6
3:5-	22,450	7.0	0.53	1.04	1.8

The interaction of benzoyl chloride with ethyl alcohol



is an obviously parallel case; it has been examined in a dozen solvents at 25° C. On converting the velocity coefficients from the units of mole fractions and hours† to those of moles per litre and seconds (equation II (23)), it is seen that the solvent effect is not a pronounced one, e.g. in carbon tetrachloride  $k$  is  $1.9 \times 10^{-5}$  and in ethyl alcohol it is  $4.2 \times 10^{-5}$ . No direct temperature coefficients are available. From the absolute magnitude of the velocity constant in the non-polar solvents, the collision theory predicts an energy of activation of 21.6 kilocalories.  $E_A$  in ethyl alcohol as solvent is 17.5, which, with the correction indicated by equation (6) of Chapter IX, gives an energy of activation of 20.9, in satisfactory agreement.

† Norris and Haines, *J. Amer. Chem. Soc.*, **57**, 1425, (1935).

### *Electrostatic effects*

We have seen, from the direct evidence afforded by experiments in non-polar solvents, and from indirect evidence afforded by other experiments, that there are certain reactions between polar molecules which proceed in solution with the same rate as they would have according to the collision theory. Although these reactions are by no means numerous, they form a basis for a discussion of the very considerable literature on other reactions between molecules in solution for which  $P$  has values differing from unity.

Our first inquiry is directed to the possible influence of the electrostatic energy of the reacting polar molecules, which is†

$$\frac{E_e}{N_0} = \frac{\mu_A \mu_B}{Dr^3} f(\theta_A, \theta_B), \quad (2)$$

and to the applicability of the collision formula

$$k_2 = Ze^{-(E+E_e)/RT}. \quad IV(3)$$

The energy of interaction of two dipoles is less than that of one dipole and an ion at the same distance apart in the same medium, and much less than the energy of interaction of two ions under the same conditions. One therefore anticipates that the electrostatic disturbances diminish as we descend the series ion-ion, ion-dipole, and dipole-dipole. In fact, if we generalize the formulae of Chapter IV, we find that the Arrhenius energy may be represented as follows:

$$E_A = \frac{1}{2}RT + E + E_e(1 - LT). \quad (3)$$

The electrostatic contribution to the temperature coefficient of the apparent energy of activation is then

$$\frac{dE_A^0}{dT} = \frac{R}{2} - E_e L^2 T, \quad (4)$$

and the electrostatic factor in the total probability term,  $P$ , at infinite dilution becomes

$$P^0 = e^{-LE_e/R} \quad (5)$$

as in equations (4) and (3) of Chapter V. Using reasonable dipole moments and dielectric constants, we see that the former effect is so small as to elude detection, and that  $P^0$ , for all variations in the angles, can never differ markedly from unity. Are we, then, to conclude that the electrostatic contribution to the energy of activation in these reactions can be neglected? The answer is a definite

† Based on equation III (12).

negative. The electrostatic energy, which accounts for most of the features of reactions between ions and which brings such harmony into the study of reactions between ions and polar molecules, cannot logically be omitted from any comprehensive treatment of reactions between polar molecules, though the manner in which it makes itself felt may not be quite the same.

One reason for the difference is that when no ions are involved there is less justification for using as the dielectric constant the value which is measured in the continuous solvent medium. The ion is permanently, though not completely, solvated even in the critical complex, and the fact that it holds on to, say, five out of six of its solvent neighbours accounts in a crude way for the success attending the use of  $D$  for all separations up to the critical one. The solvation of polar molecules is nothing like so firm, and a solute molecule,  $A$ , may freely replace one of its solvent neighbours by solute molecule,  $B$ , particularly when  $A$  and  $B$  are structurally similar to the solvent, as in the many reactions of aromatic compounds in benzene solution. With the two solutes in direct contact, a value of  $D$  near to unity and a value of  $L$  approximating to zero may be used. A more exact result is obtained by replacing  $D$  by the ratio  $3D/(D+2)$ .† The electrostatic energy of two dipoles in a medium of dielectric constant  $D$  is then

$$\frac{E_e}{N_0} = \left( \frac{D+2}{3D} \right) \frac{\mu_A \mu_B}{r^3} f(\theta_A, \theta_B). \quad (6)$$

This expression is at best an approximation, for its derivation is based on assumptions concerning the molecular model which do not tally well with the actual model. Nevertheless, it can lay claim to some experimental support. The ratio of the energies of interaction of two carboxylic acids in benzene solution and in the gaseous phase should, according to this formula, be

$$\frac{E_e(\text{benzene})}{E_e(\text{gas})} = \frac{D+2}{3D}. \quad (7)$$

Using the value of  $D$  for benzene given in Table IV(1), the ratio is found to be 0·67. The experimental values of the energies given in Chapter VI are 9·7 and 14·5 respectively, which yield a ratio of 0·68, in substantial agreement. The main service of equation (6) is that it brings home, in an approximately correct form, the undisputed fact

† Frank, *Proc. Roy. Soc., A*, 152, 174, (1935).

that the energy of interaction of two dipoles in contact and surrounded by a medium of dielectric constant,  $D$ , is greater than the energy when they are both surrounded by the same medium, and less than the energy when, as in the gas phase, neither is surrounded by the medium.

On combining equation IV (3) with this revised expression for the electrostatic interaction energy, we obtain for the bimolecular velocity coefficient of reactions between molecules with permanent dipole moments the expression

$$k_2 = Ze^{-E/RT} e^{-(D+2)/(3D)\mu_A \mu_B f(\theta_A, \theta_B)/r^3 kT} \quad (8)$$

Here  $Z$  is a constant, the dimensions of which are those of a collision frequency, which we shall provisionally regard as being independent of temperature.  $E$  is the remainder of the activation energy, of the nature of which we as yet know little; and  $r$  is the critical distance apart of the centres of the reacting dipoles. Differentiation of the logarithm of this expression with respect to the reciprocal of the dielectric capacity at constant temperature leads to the relation

$$\left[ \frac{d \ln k_2}{d(1/D)} \right]_T = -\frac{2}{3kT} \frac{\mu_A \mu_B f(\theta_A, \theta_B)}{r^3}, \quad (9)$$

which we shall later apply to our study of the solvent effects. The relation between the apparent energy of activation and the other energy terms, according to the present hypothesis, is

$$E_A = E + \frac{N_0 \mu_A \mu_B}{r^3} f(\theta_A, \theta_B) f(D, T), \quad (10)$$

where

$$f(D, T) = \frac{D+2(1-LT)}{3D} = \left[ D+2+2\left(\frac{d \ln D}{d \ln T}\right)_P \right] / 3D. \quad (11)$$

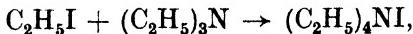
The electrostatic factor in the empirical ratio,  $P$ , at infinite dilution becomes

$$P^0 = \exp \left[ -\left( \frac{2}{D+2} \right) \frac{E_e L}{R} \right] = \exp \left[ -\frac{N_0 \mu_A \mu_B}{r^3} f(\theta) \times \frac{2L}{3DR} \right]. \quad (12)$$

Before attempting an application of these formulae we must become acquainted with some of the experimental results.

### *The Influence of the Solvent: Experimental Results*

The solvent effect was first systematically tackled by Menschutkin,<sup>†</sup> who measured, at 100° C., the rate at which ethyl iodide and triethylamine,



<sup>†</sup> Z. physikal. Chem., 6, 41, (1890).

combine in various media. His relative constants (Table 2) show that the reaction is always faster in an aromatic solvent than in the corresponding aliphatic solvent.

Table 2

	Solvent	Relative <i>k</i>
Hydrocarbons	Hexane	0·13
	Heptane	0·17
	Xylene	2·2
	Benzene	2·4
Halogen Derivatives	Propyl chloride	4·0
	Chlorobenzene	17·4
	Bromobenzene	20·3
	$\alpha$ -Bromonaphthalene	84·9
Ethers	Ethyl- <i>iso</i> -amyl ether	0·47
	Diethyl ether	0·57
	Phenetole	16·0
	Anisole	30·3
Esters	<i>Iso</i> -butyl acetate	4·3
	Ethyl acetate	16·7
	Ethyl benzoate	19·4
	<i>Iso</i> -butyl alcohol	19·4
Alcohols	Ethyl alcohol	27·4
	Allyl alcohol	32·5
	Methyl alcohol	38·0
	Benzyl alcohol	100·0
Ketones	Acetone	45·7
	Acetophenone	97·3

The 'slow' solvents are the hydrocarbons and ethers; the 'fast' solvents are the alcohols and ketones. The positive catalytic influence of the solvent thus runs roughly parallel with its general chemical reactivity—a result which justified Menschutkin in classifying the solvent influence among specific chemical effects. The same order of solvent activity has been found for some unimolecular reactions, e.g. the decomposition of xanthogenic acid,† the isomerization of camphene hydrochloride,‡ and the decomposition of trinitrobenzoic acid.§ It is roughly the same as the order of the dielectric constants—a parallelism which has also been noted in the rates of keto-enol conversions.|| The velocity of Dimroth's triazole reaction (p. 187), on the other hand, is about  $10^4$  times as great in chloroform ( $D = 4\cdot95$ ) as in water ( $D = 81\cdot7$ ).

† von Halban and Kirsch, *Z. physikal. Chem.*, **82**, 325, (1913).

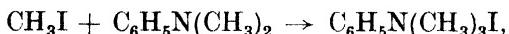
‡ Meerwein and Montfort, *Annalen*, **435**, 207, (1925); Meerwein and Ernster, *Berichte*, **55**, 2500, (1922).

§ Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc., A*, **113**, 186, (1931).

|| Stobbe, *Annalen*, **326**, 359, (1903).

More recent work on the solvent effect has naturally sought to connect it, not with the velocity coefficient itself, but with the two constants of the Arrhenius equation.

We have first to consider the accuracy ascribable to these constants in so far as they relate to reactions between polar molecules, particularly in non-aqueous solvents, where reproducibility of results is, on the whole, less satisfactory. Essex and Gelormini<sup>†</sup> measured the rate of union of methyl iodide with dimethylaniline,



and of similar reactions in various solvents by estimating the silver iodide gravimetrically after extraction. With their equilibrium data we are already familiar (p. 170). The energies obtained from their kinetic data at various temperatures and in two solvents are shown in Table 3. The reproducibility can be gauged from the first two

*Table 3*

*Apparent Energies of Activation (calories) for the Union of Methyl Iodide with Dimethylaniline at Various Temperatures*

<i>t</i> ° C.	Solvent: $\text{C}_6\text{H}_5\text{NO}_2$	Solvent: $\text{C}_6\text{H}_5\text{CH}_3\text{OH}$
15.03	12,903	14,379
15.07	12,959	14,390
25.03	12,578	14,565
34.99	13,287	14,220
44.99	13,056	14,472
Average $E_A$ at 30° C.	$12,975 \pm 500$	$14,405 \pm 160$

entries in each column, the second of which was obtained at the end of the series of experiments. An error of  $\pm 28$  calories in nitrobenzene and of  $\pm 6$  in benzyl alcohol is thus indicated at 15° C., and higher errors occur at other temperatures. The maximum value found for  $E_A$  in nitrobenzene at 35° C. is taken by the investigators as genuine, but despite the occurrence of similar maxima with other reactions in this solvent, grave doubt must remain concerning it. Drying this solvent by means of calcium chloride, as was done in these experiments, is not sufficient to secure its purity for kinetic work (p. 299).<sup>‡</sup> Seldom, however, have velocity coefficients for reactions of this type been measured with greater care.

The general effect of changing the solvent is to bring about a

<sup>†</sup> *J. Amer. Chem. Soc.*, **48**, 882, (1926).

<sup>‡</sup> I am indebted to Dr. Harry Essex for helpful communications on this and other points arising from his work.

change in both  $E_A$  and  $A$ , the two changes being in the same direction.<sup>†</sup> Increases in  $E_A$  are thus attended by increases in  $\ln A$ , though not proportionately, as with the hydrolysis of glycosides (Table III (3)). Cases are known, however, where the solvent effect

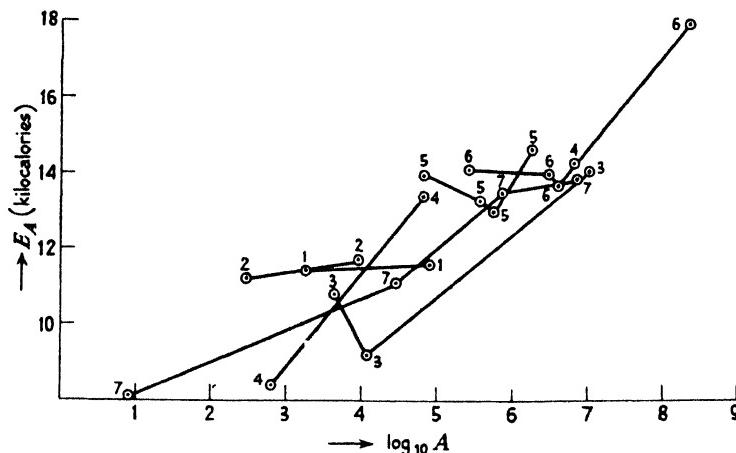


FIG. 1. The influence of solvents on the Arrhenius constants for certain reactions of amines and halides. The reference numbers are those of Table 5.

seems to be shouldered entirely on to either  $A$  or  $E_A$ . The data in Table 4 have been selected from the work of Grimm, Ruf, and Wolff<sup>‡</sup> to illustrate this specific point. In the more usual cases, when both

Table 4  
Arrhenius Constants for the Reaction  $C_2H_5I + (C_2H_5)_3N \rightarrow (C_2H_5)_4NI$  in Selected Solvents

Solvent	$k_{100^\circ C.} \times 10^6$	$E_A$ (kilocal.)	$A$
Cyclo- $C_6H_{12}$	1.00	17.1 $\pm$ 1.0	$1.14 \times 10^5$
Ortho- $Cl_2C_6H_4$	250	13.04 $\pm$ 0.26	$1.14 \times 10^5$
$C_6H_5CN$	1,120	11.9 $\pm$ 0.3	$1.04 \times 10^6$
$C_6H_5I$	39.8	11.4 $\pm$ 0.3	$1.83 \times 10^3$
$(C_2H_5)_2O$	116	11.65 $\pm$ 0.51	$8.28 \times 10^3$
$C_6H_5NO_2$	1,380	11.6 $\pm$ 0.3	$81.8 \times 10^3$

$E_A$  and  $A$  vary, the greater part of the velocity change is due to changes in  $E_A$ . Some representative results, chosen because of their accuracy and the use of solvents in common, have been brought together in Table 5, and are shown graphically in Fig. 1. The general

<sup>†</sup> *Chem. Rev.*, 10, 230, (1932).

<sup>‡</sup> *Vide infra.*

Table 5

*Reactions of Amines and Halides in Various Solvents ( $E_A$  in kilocalories;  $A$  in litres/gram mole-second)*

Reference	Solvent:	$C_6H_6$ ( $D = 2.3$ )		$C_6H_5OH$ ( $D = 25.0$ )		$(CH_3)_2CO$ ( $D = 31.0$ )		$C_6H_5NO_2$ ( $D = 35.8$ )	
		$E_A$	$\log_{10} A$	$E_A$	$\log_{10} A$	$E_A$	$\log_{10} A$	$E_A$	$\log_{10} A$
(1)	$(C_2H_5)_3N + C_6H_5I$	11.4	3.26	—	—	—	—	11.6	4.91
(2)	$(C_2H_5)_3N + C_6H_5Br$	11.7	3.96	—	—	—	—	11.2	2.47
(3)	$(C_2H_5)_3N + C_6H_5CH_2Cl$	10.8	3.62	14.1	6.99	—	—	9.2	4.07
(4)	$C_6H_5N + C_6H_5CH_2Cl$	13.4	4.81	14.3	6.80	—	—	8.4	2.81
(5)	$C_6H_5N + CH_3:CHCH_2Br$	13.95	4.81	14.65	6.25	13.30	5.55	13.0	5.74
(6)	$C_6H_5N + CH_3I$	14.1	5.41	18.0	8.32	14.0	6.49	13.7	6.59
(7)	$C_6H_5NH_2 + CH_3COCH_3Br$	8.1	0.92	13.9	6.83	11.1	4.46	13.5	5.84

- (1) Grimm, Ruf, and Wolff, *Z. physikal. Chem.*, **B**, **13**, 301, (1931). Error of  $\pm 0.3$  in  $E_A$  assessed by the investigators.
- (2) Hemptinne and Bekaert, *ibid.*, **28**, 225, (1899). Error in  $E_A$  difficult to assess, but may be as high as  $\pm 2.0$ . Estimated  $dE_A/dT$  is as high as  $+155 \pm 25$ .
- (3, 4) Muchin, Ginsberg, and Moissejeva, *Ukraine Chem. J.*, **2**, 136, (1926).
- (5) Hawkins, *Trans. Chem. Soc.*, **121**, 1170, (1922). Errors in  $E_A$  estimated, successively, as  $\pm 0.02$ ,  $\pm 0.23$ ,  $\pm 0.16$ , and  $\pm 0.62$ .
- (6) Pickles and Hinshelwood, *ibid.*, 1353, (1936); Fairclough and Hinshelwood, *ibid.*, 1573, (1937).
- (7) Cox, *ibid.*, **119**, 142, (1921).

tendency for one of the constants to increase if the other one does so is at once apparent. There is also a tendency for the gradient  $dE_A/d\ln A$  to increase for large values of either constant, as one would expect, on general grounds. How far the curvature may be ascribed to a proportionality to the temperature,  $T$ , is not certain. Hinshelwood has found in certain cases that  $\ln A$  varies linearly as  $E_A^2$ , and has offered a theoretical explanation (p. 286). There are some faint indications of minima in the various curves.

The reactions listed in Table 5, with the exception of the last one, have been examined also in mixed solvents, such as binary mixtures of hydrocarbons and ketones. The variety of observations includes continuous variations of the constants with composition of the solvent, maxima, minima, double maxima, and a maximum and minimum, and have formed the basis of many discussions which it is the object of this paragraph to introduce rather than to replace.

#### *The Influence of the Dielectric Capacity of the Medium*

There appears to have been no formal treatment of the effect of the dielectric constant,  $D$ , on reactions between molecules in solution,

although parallelisms between  $D$  and the bimolecular velocity coefficient,  $k_2$ , have frequently been noted, especially in the earlier work.

On the simple assumption that the electrostatic component of the activation energy is inversely proportional to the dielectric constant,

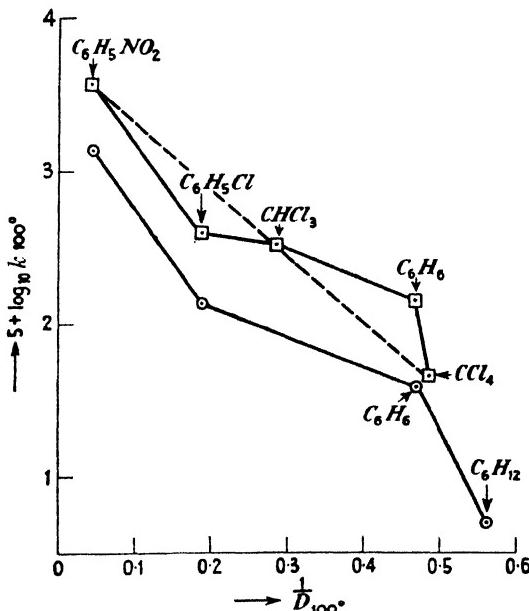


FIG. 2. The influence of the dielectric constant on the velocity of the reactions between ethyl iodide and triethylamine ( $\circ$ ) and between methyl iodide and pyridine ( $\square$ ).

according to equation (2), we derive the following relationship between  $k_2$  and  $D$  at a constant temperature:

$$\left[ \frac{d \ln k_2}{d(1/D)} \right]_T = -\frac{1}{RT} \frac{N_0 \mu_A \mu_B f(\theta_A, \theta_B)}{r^3}; \quad (13)$$

which, like other relationships to be examined in this section, may be illustrated with reference to the reactions between pyridine and methyl iodide† and between triethylamine and ethyl iodide‡ in those solvents for which the constants of Table IV (1) are known. From an examination of the data of Table 6 and of Fig. 2, we see that, despite certain irregularities, there is a clear tendency for the solvent to affect the velocity of reaction in accordance with our elementary electrostatic considerations. At least some of the solvent

† Pickles and Hinshelwood, *loc. cit.*

‡ Grimm, Ruf, and Wolff, *loc. cit.*

Table 6

*The Influence of the Dielectric Constant on Two Reactions between Polar Molecules*

Solvent	$D_{100^\circ\text{C}}$	(1/D)	Reaction:	$(\text{C}_2\text{H}_5)_3\text{N} + \text{C}_2\text{H}_5\text{I}$	$\text{C}_6\text{H}_5\text{N} + \text{CH}_3\text{I}$
				$5 + \log_{10} k_{100^\circ}$ (litres/gm. mol.-sec.)	
$n\text{C}_6\text{H}_{12}$	1.79	0.560		0.70	—
$\text{CCl}_4$	2.07	0.483		—	1.65
$\text{C}_6\text{H}_6$	2.13	0.470		1.60	2.15
$\text{CHCl}_3$	3.47	0.288		—	2.525
$\text{C}_6\text{H}_5\text{Cl}$	5.28	0.189		2.14	2.60
$\text{C}_6\text{H}_5\text{NO}_2$	23.6	0.043		3.14	3.57

effects must be electrostatic in origin. On the same basis we have shown that

$$E_A = \frac{1}{2}RT + E + E_e(1 - LT), \quad (3)$$

which, in the present example, may also be written as follows:

$$E_A = \frac{1}{2}RT + E + \frac{N_0 \mu_A \mu_B f(\theta_A, \theta_B)}{r^3} \left( \frac{1 - LT}{D} \right). \quad (14)$$

In Fig. 3 is shown the dependence of the Arrhenius energy of activation on the function  $(1 - LT)/D$ . Data for the pyridine-methyl iodide reaction are reproduced by the linear equation

$$E_A = 13600 + 7200 \left( \frac{1 - LT}{D} \right). \quad (15)$$

The apparent and the true energies of activation without a solvent medium are thus 20,800 and 13,200 calories respectively. By giving  $f(\theta_A, \theta_B)$  a value of 2, we obtain

$$r = 2.296 \text{ \AA}. \quad (16)$$

The magnitude of the electrostatic energy is, of course, obtainable without making such an assumption, and is shown in Table 7. These results indicate that the electrostatic contribution is a positive quantity, denoting repulsion, and that, particularly in the non-dissociating solvents, it may be quite an appreciable fraction of the total energy of activation.

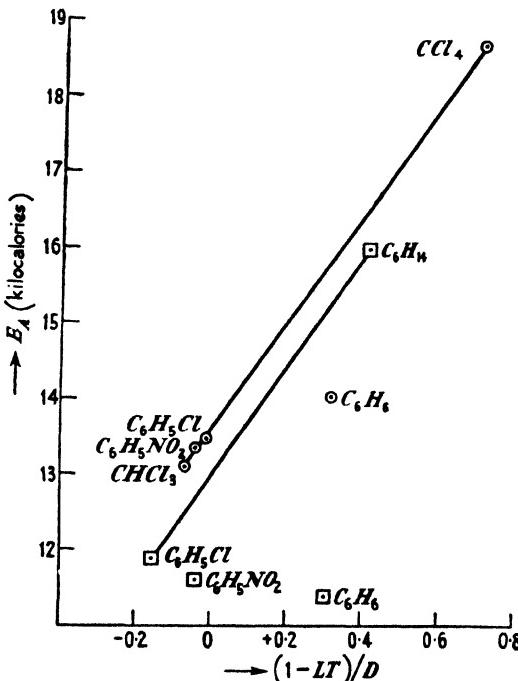
The simple assumption upon which these calculations are based may be improved by regarding the electrostatic energy as being proportional to  $(D+2)/3D$ , rather than to  $1/D$ . On differentiating  $\ln k_2$  with respect to this function, we now find that  $N_0 \mu_A \mu_B f(\theta_A, \theta_B)/r^3$  is about 11,000 calories, which, if the angular function is again taken as 2, leads to a value of 2.00 Å. for  $r$ . A better test of the revised

Table 7

*The Evaluation of the Electrostatic Contribution to the Energy of Activation of the Reaction between Pyridine and Methyl Iodide at 100° C. (Energies in calories/gram mole)*

Solvent	$D_{100^\circ}$	$(1 - LT)/D_{100^\circ}$	$E_s$	$E_A$	$E$
$C_6H_5NO_2$	23.6	-0.04	310	13,700	13,620
$C_6H_5Cl$	5.28	-0.015	1,390	13,900	13,640
$CHCl_3$	3.47	-0.07	2,110	13,200	13,340
$C_6H_6$	2.13	+0.315	3,440	14,100	11,430
$CCl_4$	2.07	+0.71	3,540	18,700	15,890

expression, however, would appear to be provided by equation (10), which, when applied to the reactions between ethyl iodide and



○ The reaction between methyl iodide and pyridine.

□ The reaction between ethyl iodide and triethylamine.

FIG. 3. The dependence of the apparent energy of activation on  $(1 - LT)/D$ .

triethylamine and between methyl iodide and pyridine (Table 8 and Fig. 4) leads, respectively, to the following numerical results:

$$\left. \begin{aligned} E_A &= 7200 + 14700f(D, T) \\ E_A &= 8000 + 19640f(D, T) \end{aligned} \right\} \quad (17)$$

and

The latter equation indicates a value of  $1.29 \text{ \AA}$ . for  $r$ . The critical separation thus lies in the region  $1.65 \pm 0.35 \text{ \AA}$ . The electrostatic contribution to the energy of activation, on this basis, is a considerable one, leaving an energy of only about 5 to 6 kilocalories to be

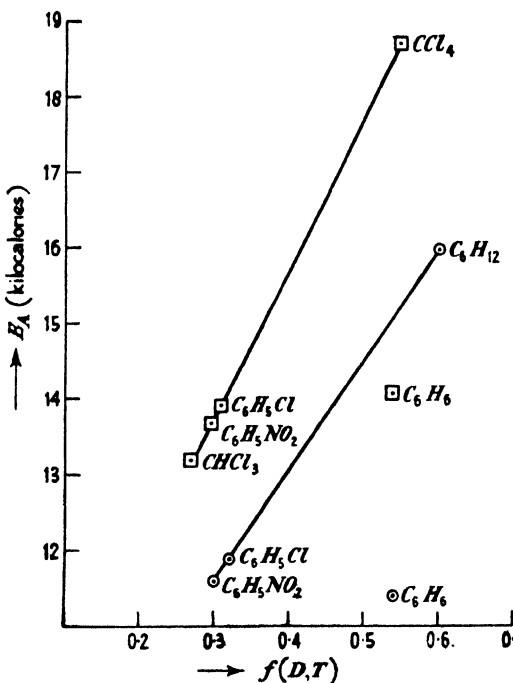


FIG. 4. The influence of the dielectric constant on the Arrhenius term  $E_A$  for reactions between ethyl iodide and triethylamine ( $\odot$ ) and between methyl iodide and pyridine ( $\square$ ).

Table 8

*The Dependence of  $E_A$  on a Function of the Dielectric Constant of the Medium.  
(Energies in kilocalories per gram mole)*

Solvent	$D + 2(1 - LT)$	Reaction between C <sub>2</sub> H <sub>5</sub> I and (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		Reaction between CH <sub>3</sub> I and C <sub>6</sub> H <sub>5</sub> N		
		$3D$	$E_A$	$E_A$	$E_s$	$E$
CCl <sub>4</sub>	0.55	—	—	18.7	12.9	5.8
C <sub>6</sub> H <sub>12</sub>	0.60	16.0	—	—	—	—
C <sub>6</sub> H <sub>6</sub>	0.54	11.4	—	14.1	12.7	1.4
CHCl <sub>3</sub>	0.27	—	—	13.2	10.3	2.9
C <sub>6</sub> H <sub>5</sub> Cl	0.31	11.9	—	13.9	9.0	4.9
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.30	11.6	—	13.7	7.1	6.6

accounted for by factors which cannot be directly connected with the specific inductive capacity of the medium. There appears to be, on the whole, a decided proportionality between the observed energy of activation and the function  $f(D, T)$ . Thus the increase of 5,500 calories found in  $E_A$  on passing from chloroform to carbon tetrachloride—a rather remarkable difference for such a slight change in solvent composition—can be fully accounted for.

It is not possible to decide on kinetic evidence alone which of the two expressions which we have employed represents more accurately the effect of the medium on the electrostatic energy. Both are approximate formulae. Their adoption, nevertheless, has been profitable were it only to indicate what little progress has yet been made in this field of inquiry.

### *The Influence of the Viscosity of the Medium*

There is definite evidence that the velocity of numerous reactions in solution is linked in some way with the viscosity of the solvent, but no general relationship between them has been established. It has been argued that the frequency of binary collisions in solution may be inversely proportional to the free space,  $v_f, \dagger$  or to  $v_f^2, \ddagger$ . According to the well-known theory of Batshinski, $\ddagger$  it would then follow that the collision frequency is directly proportional to the viscosity itself, or to the square of the viscosity. Macleod $\parallel$  has shown, however, that the relationship between free space and viscosity in liquids is not so simple as had at one time been supposed, and the improved equation proposed by him has been coupled with the general statistical formulae for gases in order to give the form of laws which may reasonably be expected to apply to solutions. $\ddagger\ddagger$  The pursuit of this treatment at present appears premature.

It is by no means a simple matter to discover experimentally in what way the velocity of chemical reactions and the viscosity of even apparently inert media are related, for, as we have previously explained (p. 152), it is seldom possible to effect a change in one variable without bringing about a change in another. We may, for example, imagine that by measuring the rate of reaction at various

$\dagger$  Jowett, *Phil. Mag.*, **8**, 1059, (1929).

$\ddagger$  Norrish and F. P. Smith, *Trans. Chem. Soc.*, 129, (1928).

$\ddagger$  *Z. physikal. Chem.*, **84**, 643, (1913).

$\parallel$  *Trans. Faraday Soc.*, **32**, 872, (1936).

$\ddagger\ddagger$  Moelwyn-Hughes, *ibid.*, **34**, 91, (1938).

temperatures we can directly derive the energy required by the molecules before they react. Such a direct answer, however, is not in general provided; when the energy of activation consists even partly of electrostatic terms, the change in temperature acts in at least two ways. It increases the number of molecules possessing the necessary energy, and, by lowering the dielectric constant, increases also the electrostatic energy of interaction of two solute molecules at a fixed distance apart. The similar difficulty in the case of viscosity may to some extent be circumvented by seeking a variable which influences both the reaction velocity and the viscosity. Pressure is one such variable. The effect of great external pressures on the viscosity of liquids is, with few exceptions, to enhance it.<sup>†</sup> Also, with very few exceptions, the effect of great pressures on the velocity of reactions in solution is to enhance it, as we shall see in greater detail in Chapter XI. Parallelisms of this kind, though they may ultimately prove nothing, are always worth following.

Let it be supposed that the velocity constant,  $k$ , can be expressed under constant temperature conditions by an equation of the form

$$k = C(\eta)\nu, \quad (18)$$

where  $\nu$  is a number, and  $C$ , though not constant, is but a slowly varying function of  $\eta$ . For a given reaction measured at a constant pressure,  $P$ , and at some reference pressure, say that of the atmosphere, we then have the ratio

$$\frac{k_P}{k_1} = \left( \frac{C_P}{C_1} \right) \left( \frac{\eta_1}{\eta_P} \right)^\nu. \quad (19)$$

Differentiation gives us the relation

$$\left[ \frac{d \ln(k_P/k_1)}{d \ln(\eta_P/\eta_1)} \right]_T = \left[ \frac{d \ln(C_P/C_1)}{d \ln(\eta_P/\eta_1)} \right]_T + \nu, \quad (20)$$

in which, by hypothesis, the first term is relatively small. If equation (18) has any validity we should therefore expect the logarithm of the relative velocity to vary almost linearly with respect to the logarithm of the relative viscosity. When we compare velocities found by Gibson, Fawcett, Perrin, and Williams<sup>‡</sup> for a variety of reactions under great external pressures, with the liquid viscosities obtained, sometimes by slight extrapolation, from Bridgman's monograph,<sup>§</sup>

<sup>†</sup> Bridgman, *The Physics of High Pressures*, Bell, London, (1931).

<sup>‡</sup> Proc. Roy. Soc. A, 150, 223, (1935); 154, 684, (1936).

<sup>§</sup> Loc. cit.

we see that such a relationship undoubtedly exists (Table 9 and Fig. 5). Despite a marked tendency to an initial curvature, the wider reaches of pressure indicate an approximately linear relationship with the

Table 9

*A Comparison of the Relative Rate of Chemical Change with the Relative Viscosity of the Medium for Certain Reactions in Solutions under Great External Pressures*

$P$ (atmospheres)	$\log_{10}(k_P/k_1)$	$\log_{10}(\eta_P/\eta_1)$	$\nu$
1. The reaction between ethyl iodide and sodium ethoxide in ethyl alcohol at 30° C.			
1	0	0	
2,980	0.201	0.480	
5,000	0.315	0.720	0.2
8,500	0.395	1.060	
12,000	0.455	1.390	
2. The reaction between sodium acetate and sodium hydroxide in water at 40° C.			
1	0	0	
2,980	0.322	0.088	2.0
7,600	0.713	0.263	
12,000	0.915	0.391	
3. The reaction between ethyl alcohol and acetic anhydride in toluene at 40° C.			
1	0	0	
3,000	0.652	0.70	0.9
5,000	0.860	1.11	
8,500	1.579	1.70	
4. The reaction between ethyl iodide and pyridine in acetone at 30° C.			
1	0	0	
2,975	0.857	0.488	1.5
5,000	1.172	0.720	
8,500	1.655	1.028	
5. The reaction between acetic anhydride and pure liquid ethyl alcohol at 20° C.			
1	0	0	
1,000	0.275	0.158	1.9
2,000	0.595	0.332	
3,000	0.870	0.486	

very rough values of  $\nu$  given in Table 9. Without entering into detail, we may say that there is little ground for concluding that the Hecht reaction is seriously affected by the viscosity, and that, in the other cases, the velocity constant over a very considerable pressure range is proportional to the viscosity raised to a power lying between 1 and 2. These conclusions are opposed to those obtained by comparing directly the rates of reaction with the viscosities of the medium.

On such a basis the rate of formation of sulphonium salts is apparently inversely related to the viscosity.<sup>†</sup>

The problem can be viewed from a slightly different angle by

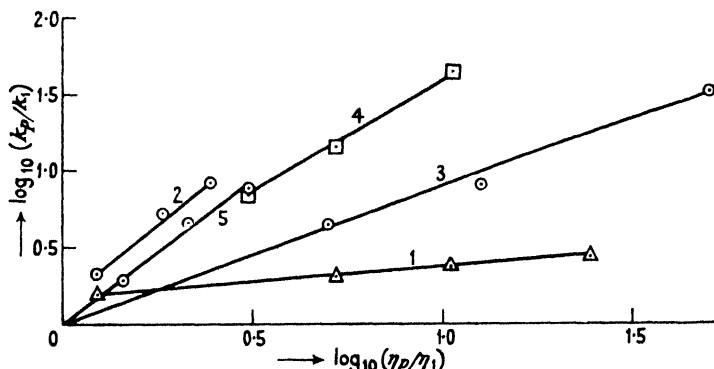


FIG. 5. The relative velocity of reactions in solution under great external pressures, plotted as a function of the relative viscosity of the solvent.

inquiring into the justification of computing an energy of activation on the assumption, implicit in equation (1), that  $E$  is  $f(T, \eta)$ . The difference between this energy and  $E(T, P)$  is

$$E_\eta - E_P = -RT^2 \left( \frac{d\eta}{dT} \right)_P \left( \frac{dP}{d\eta} \right)_T \left( \frac{d \ln k}{dP} \right)_T. \quad (21)$$

Numerical values of the first differential term have been given in Table 1 of Chapter I; the second differential coefficients have been derived from Bridgman's tables; and the third from the results of Gibson and his fellow workers. The only very marked difference between  $(E_\eta - E_P)$  thus computed and Guzman's  $B$  is found to relate to reactions in aqueous solution. The correction for the inversion of cane sugar is in an interesting direction, though possibly misleading in magnitude because the pressure coefficient of the viscosity of water at this temperature is notoriously complicated. The correction for the last reaction in Table 10 is roughly twice as great as  $B$ , indicating, as did our previous discussion, that  $v$  is approximately 2. The results emphasize chiefly that corrections based on the very elementary treatment given in Chapter IX are not only qualitatively right, but are not far from being quantitatively correct. Thus, for example, the first corrected value ( $E_A + B$ ) published for reaction 3 was 21.21.<sup>‡</sup>

<sup>†</sup> Svesnikov, *Comptes rendus de l'Académie des Sciences de l'U.R.S.S.*, III (12), 61, (1936).

<sup>‡</sup> Moelwyn-Hughes and Rolfe, *Trans. Chem. Soc.*, 241, (1932).

The rate of this reaction could, therefore, have been computed by assuming  $k$  to be proportional to the viscosity at all pressures.

Table 10

*The Evaluation of Energies of Activation, assumed to be  $f(\eta, T)$*

Reaction	Solvent	$E_P$ (kilo- cals.)	$RT \left( \frac{d \ln k}{d P} \right)_T$ (c.c.)	$RT^2 \left( \frac{d \ln \eta}{dT} \right)_P$ (kilocalcs.)	$\left( \frac{dP}{d \ln \eta} \right)_T$ (dynes/cm. <sup>2</sup> )	$E_\eta - E_P$	$E_\eta$
1. $C_6H_5N + C_6H_5I$	$(CH_3)_2CO$	14.4	16.4	1.6	$1.56 \times 10^8$	1.62	16.0
2. $C_6H_5ONa + C_6H_5I$	$C_6H_5OH$	20.8	4.3	3.2	$1.79 \times 10^8$	0.98	21.8
3. $C_6H_5OH + (CH_3CO)_2O$	$C_6H_5OH$	17.6	15.9	3.2	$1.79 \times 10^8$	3.62	21.2
4. $C_6H_5OH + (CH_3CO)_2O$	$C_6H_5CH_3$	15.3	10.5	2.1	$1.33 \times 10^8$	1.16	16.4
5. $(CH_3)(C_6H_5)(C_6H_5)$ $(C_6H_5CH_3)NBr$	$CHCl_3$	29.7	-3.3	1.4	$1.885 \times 10^8$	-0.33	29.3
6. $C_6H_5O_2^- + H_3O^+$	$H_2O$ at 16° C.	26.0	2.5	4.4	$2.30 \times 10^{10}$	10.5	36.5
7. $CH_3Cl + COONa +$ $+ NaOH$	$H_2O$ at 80° C.	22.7	6.2	3.2	$+1.20 \times 10^{10}$	7.98	30.7

### Constitutional Effects

It would be inappropriate in this work to deal at any great length with the extensive researches which have been carried out to determine the influence of molecular constitution on the velocity of bimolecular reactions between polar molecules in solution. Some reference to their origin and particularly to the clarification which has resulted from the recent recognition of the importance of the electrostatic effect may, however, be not out of place.

Some of the earlier researches, especially on the kinetics of reactions between halides and amines† were dominated by the notion that the energy of activation could be resolved into components for each reactant; and, although the idea could not always be quantitatively substantiated, the exploration of its consequences proved to be of great interest. It brought home, in the first place, the recognition that 'alteration in activation energy is a more truthful expression of the effects of substituents on reactivity than is the velocity' coefficient itself.‡ It revealed, in the second place, certain regularities in the effects of substituents in the *ortho*, *meta*, and *para* positions in the benzene ring, which, on the whole, though not universally, conformed with independently developed notions of organic reactivity. The postulated electron drifts (p. 142) are found by experiment to be attended by energy changes so small as to be often too difficult to measure. Further regularities also slowly emerged from a consideration of the constants  $A$  and  $E_A$  of the Arrhenius equation, considered in the light of the collision theory. Thus, for example, the greater

† Peacock, *Trans. Chem. Soc.*, **127**, 2177, (1925).

‡ *Idem*, *J. Phys. Chem.*, **31**, 535, (1927).

rate of reaction of trimethylamine, compared with tri-*iso*-amylamine, towards a common halide in a common solvent† is fully reflected in the smaller energy ( $\Delta E = -450$  calories). With a wider range of organic bases, however, it becomes clear from the results of Hirniak‡ that the millionfold range in velocities anticipated from the change in apparent energies of activation, is not in fact found,§ and that structural changes here, as in so many other cases, are attended by unidirectional variations in the two constants of the equation of Arrhenius.

The fact that any genuine energy change which may be associated with the introduction of a new radical is often smaller than the error in experiment or the change due to other effects, such as dilution,|| has driven some investigators to despair of finding any quantitative regularity in the effects of substituents on the velocity of reaction. Olivier,†† for example, reviewing his own data on the hydrolysis of benzyl chloride and 24 of its *ortho*, *meta*, and *para* derivatives in aqueous acetone solution, strikes this unusually pessimistic note:

'En considérant les énergies d'activation ( $E_A$ ) et les constantes d'action ( $A$ ) par rapport à la constitution de la molécule, on constate que maintenant il n'y a plus aucune régularité à découvrir dans les chiffres; on se trouve pour ainsi dire en présence d'un chaos. Par exemple, un groupe positif (le méthyle) en position para et un atome négatif (le chlore) dans la même position influencerait la polarité de la molécule de la même manière, ainsi qu'on le constate tout de suite en comparant les énergies d'activation des deux composés en question à celle du chlorure de benzyle lui-même.'

On the other hand, there have not been lacking the excessively exuberant schools of investigators who cheerfully propound theories to account for alleged energy changes which are, in fact, smaller than the errors in their measurement. A midway course is cautiously steered by E. G. Williams and Hinshelwood,‡‡ who, examining the reactions



† Preston and Jones, *Trans. Chem. Soc.*, **101**, 1912, (1930).

‡ *Tables Annuelles*, **2**, 508, (1911). § *Trans. Chem. Soc.*, 1576, (1933).

|| A decrease in velocity of 20 per cent. and an increase in  $E_A$  of about 500 calories frequently attend a doubling of the concentration in reactions of the Menschutkin type. See Rheinlander, *Trans. Chem. Soc.*, **123**, 3099, (1923); van Optall, *Rec. trav. chim. Pays-bas*, **52**, 901, (1933); Peacock, *J. Phys. Chem.*, **40**, 669, (1936).

†† *Rec. trav. chim. Pays-bas*, **56**, 247, (1937).

‡‡ *Trans. Chem. Soc.*, 1079, (1934); see also Newling, Staveley, and Hinshelwood, *Trans. Faraday Soc.*, **30**, 597, (1934).

in benzene solution, found that the apparent energies of activation,  $E_A$ , are related to the dipole moment of the parent compounds  $C_6H_5X$  or  $C_6H_5Y$  in much the same way as are the energies of activation of the nuclear chlorination of substituted phenolic ethers, the enolization of substituted acetophenones, and the saponification of substituted benzoic esters (pp. 140, 143, and 141). Dipole-dipole effects, in other words, are as discernible as ion-dipole effects. In a summary of data relating to these and to certain other reactions which can profitably be examined in the same way (Table 11), we

Table 11

*The Influence of Substituents, in the para Position, on the Constants  $E_A$  (kilocalories) for some Reactions between Polar Molecules*

Reference	Reaction	Solvent	Substituent (X) in the para position			
			CH <sub>3</sub>	H	Cl	NO <sub>2</sub>
(1)	X. $C_6H_5CH_3Cl + C_6H_5OH$	$H_2O-C_6H_5OH$	20.4	19.9	21.6	22.0
(2)	X. $C_6H_5COCl + C_6H_5OH$	$(C_6H_5)_2O-C_6H_5OH$	15.9	12.5	13.8	11.1
(3)	X. $C_6H_5COCl + C_6H_5NH_2$	$C_6H_6$	7.8	7.35	7.0	5.9
(4)	X. $C_6H_5NH_2 + C_6H_5COCl$	$C_6H_6$	6.8	7.35	7.6	11.8
(5)	X. $C_6H_5CH_3Br + C_6H_5N$	$(CH_3)_2CO$	12.5	12.5	12.7	12.3
(6)	X. $C_6H_5NH_2 + 2:C_6H_5Cl$	$C_6H_5OH$	10.1	11.2	12.3	—

(1) Olivier, Table 1.

(2) Branch and Nixon, *J. Amer. Chem. Soc.*, **58**, 2499, (1936).

(3, 4) E. G. Williams and Hinshelwood, and Newling, Staveley, and Hinshelwood, *loc. cit.*

(5) Baker and Nathan, *Trans. Chem. Soc.*, **519**, 1840, (1935); W. C. Davies, *ibid.*, 1865, (1938).

(6) Peacock, *loc. cit.*

shall restrict attention to the effect of substituents in the *para* position. Using the dipole moments of Table V, 15, we then find the curves shown in Fig. 6. No significance attaches to the signs of the tangents, as  $\mu(C_6H_5X)$  has merely been given a conventional sign for both reactants. It should, perhaps, be pointed out that, since the seats of reaction in both reactants are at ends of the molecule remote from the position of the substituted group, different signs attach to the moments of one and the same substituent in the two reactants. When this is allowed for, the two bottom curves, for example, are seen not to cross each other but to be parts of a continuous curve.

Provided the electrostatic energy of the interaction of the two dipoles contributes to the energy of activation, we may, regardless

of the exact dependence of this energy on the dielectric constant, express the relation between the Arrhenius energy and the electrostatic energy in the form

$$E_A = E + \frac{N_0 \mu_A \mu_B}{r^3} f(\theta_A, \theta_B) f(D, T), \quad (10)$$

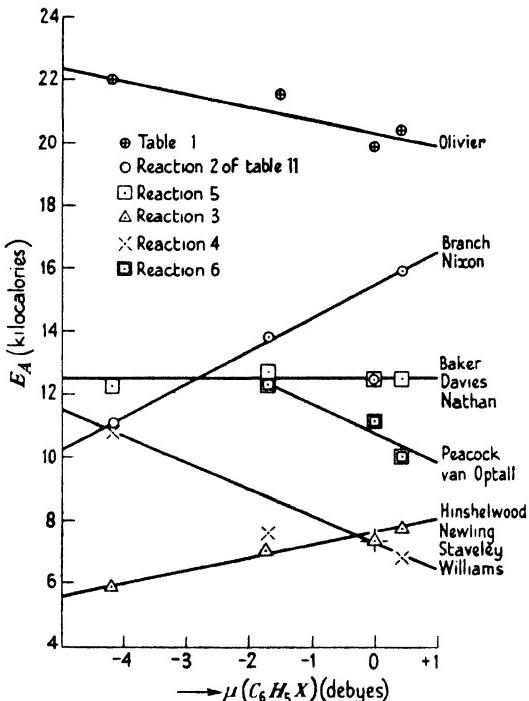


FIG. 6. The influence of *para* substituents on the Arrhenius term  $E_A$  for certain reactions between polar molecules in solution.

of which equations (2) and (6) are special cases. Expressing the energies in calories per gram mole,  $r$  in Ångstrom units, and  $\mu$  in Debye units, we have

$$E_A = E + \frac{14450}{r^3 (\text{\AA.})} \mu_A \mu_B (\text{Debyes}) f(\theta_A, \theta_B) f(D, T). \quad (10a)$$

For a series of similar reactions in the same solvent, therefore, we anticipate a linear relationship between  $E_A$  and the product of the two moments. This anticipation is amply fulfilled. Using the energies of activation obtained by Winkler and Hinshelwood† and by Williams

† *Trans. Chem. Soc.*, 1147, (1935).

and Hinshelwood,<sup>†</sup> and, as far as possible, the dipole moments measured in inert solvents by Partington and Cowley,<sup>‡</sup> we obtain, from the data summarized in Table 12, the linear plots shown in Fig. 7. The curves correspond to the equations

$$E_A = 5600 + 2840\mu_A\mu_B \text{ (debyes)} \quad (22)$$

and

$$E_A = 5800 + 390\mu_A\mu_B \text{ (debyes).} \quad (23)$$

Table 12

*Dipole Moments and Apparent Energies of Activation (calories) of Certain Bimolecular Reactions between Undissociated Molecules in Benzene Solution*

Reactants		$\mu_{\text{base}} \times 10^{18}$	$\mu_{\text{halide}} \times 10^{18}$	$\mu_A \mu_B \times 10^{36}$	$E_A$
Base	Halide				
(CH <sub>3</sub> ) <sub>3</sub> N + CH <sub>3</sub> I		0.82	1.41	1.16	8,790
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N + CH <sub>3</sub> I		0.90	1.41	1.27	9,300
C <sub>6</sub> H <sub>5</sub> N + CH <sub>3</sub> I		2.16	1.41	3.05	14,250
C <sub>6</sub> H <sub>7</sub> N + CH <sub>3</sub> I		2.19	1.41	3.09	14,350
C <sub>6</sub> H <sub>6</sub> N + CH <sub>3</sub> I		2.16	1.41	3.05	14,250
C <sub>6</sub> H <sub>6</sub> N + C <sub>2</sub> H <sub>5</sub> I		2.16	1.78	3.76	15,760
C <sub>6</sub> H <sub>5</sub> N + C <sub>6</sub> H <sub>5</sub> I		2.16	1.84	3.98	16,100
C <sub>6</sub> H <sub>5</sub> N + C <sub>6</sub> H <sub>5</sub> I		2.16	1.95	4.21	18,000
p-CH <sub>3</sub> , C <sub>6</sub> H <sub>4</sub> , NH <sub>2</sub> + C <sub>6</sub> H <sub>5</sub> COCl		1.31	2.5	3.3	6,800
H, C <sub>6</sub> H <sub>5</sub> , NH <sub>2</sub> + C <sub>6</sub> H <sub>5</sub> COCl		1.53	2.5	3.8	7,350
p-Cl, C <sub>6</sub> H <sub>5</sub> , NH <sub>2</sub> + C <sub>6</sub> H <sub>5</sub> COCl		2.95	2.5	7.4	7,600
p-NO <sub>2</sub> , C <sub>6</sub> H <sub>5</sub> , NH <sub>2</sub> + C <sub>6</sub> H <sub>5</sub> COCl		6.2	2.5	15.4	11,800

As both sets of reactions have been measured in the same solvent, we may take  $f(D, T)$  as having a common value. The difference in the coefficients of  $\mu_A \mu_B$  must therefore be due to differences in the values of  $r$  or of  $f(\theta_A, \theta_B)$  or of both. The ratio of the coefficients is seen to be about 7 (note the two scales of abscissae). If the angular function were the same for the two sets of reactions, we would conclude that the critical separation of the dipoles in the benzoylation reactions is about twice as great as in the quaternary salt formations. On the other hand, the critical distances may be about the same for both sets, while  $f(\theta_A, \theta_B)$  is less for the benzoylation. Some of the observed effect must be due to the latter cause, for it is known that the total moment of benzoyl chloride, unlike that of pyridine, does not lie along the principal axis of symmetry of the molecule. By extending such arguments one can, as with reactions between ions

<sup>†</sup> *Trans. Chem. Soc.*, 1079, (1934).

<sup>‡</sup> *Ibid.*, 977, (1938).

and dipoles (p. 122), infer the relative directions of approach of the reacting molecules.

Some assistance in deciding the form of the function  $f(D, T)$  may also be obtained from these results. We have, in principle, the possibilities that the dielectric constant does not enter into the

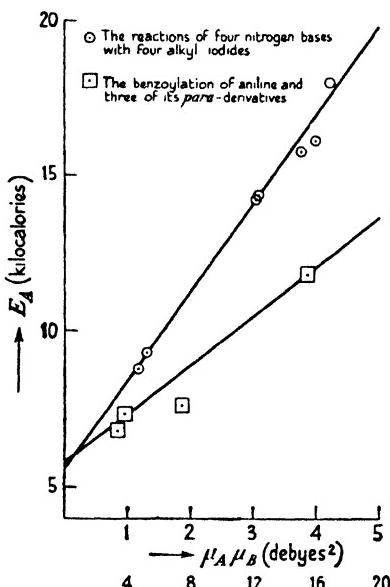


FIG. 7. The dependence of the apparent energy of activation, in benzene solution, on the product of the dipole moments of the reactants.

problem, as the molecules are in contact when they react; that it enters in the simple form  $1/D$  if the molecules are still partly separated by the solvent medium; and that it enters as  $(D+2)/3D$  because the molecules at all stages are surrounded by the medium. The numerical values of  $f(D, T)$  to be considered are given in Table 13, along with the values of  $f(\theta_A, \theta_B)/r^3$  found by adopting them, in turn, for the reactions between bases and halides in benzene solution. A detailed analysis of the combined data (equations (15), (17), and (22)) for the pyridine-methyl iodide reaction in various solvents and of homologous reactions in benzene solution can be shown to lead, without prejudice to the angular function, to a value of 0.44 for  $f(D, T)$ . This is evidence, as far as it goes, for accepting the third of the possibilities under examination. The critical separation of the

Table 13

*Numerical Estimates of the Critical Separation of Dipoles in the Reaction between Halides and Nitrogen Bases in Benzene Solution*

$f(D, T)$	$f(D, T)_{100^\circ\text{C.}}$	$f(\theta_A, \theta_B)/r^3 (\text{\AA.})$	$r (\text{\AA.}), \text{assuming } f(\theta_A, \theta_B) = 2$
1	1	0.20	2.17
$(1-LT)/D$	0.315	0.62	1.47
$D+2(1-LT)$	0.54	0.54	1.77
$3D$			

dipoles, according to the various hypotheses, is also included in Table 13. The value of 1.77 Å. confirms that of  $1.65 \pm 0.35$  derived from an examination of the solvent effect only (p. 215). More satisfactory results would naturally be found if we were in a position to use the dipoles of the actual groups reacting, but the method of analysis need not be altered.

Constitutional effects on the velocity of reactions between polar molecules are not, of course, limited to the electrostatic energy of the dipoles. Many other forces come into play.

#### *The Role of Interaction Energies other than those due to Permanent Molecular Polarity*

When molecules are pressed close together, as they often are in solution, and always in critical complexes, forces other than those which we have discussed in the preceding sections are called into action. Strong forces of attraction, for example, varying inversely as the seventh power of the distance, arise due to mutual induction and to general dispersion. There are few reactions yet studied where any allowance has been made for the influence of these forces. Wassermann† has shown that they not only feature prominently in the addition of *cyclo*-pentadiene to benzoquinone, but probably determine the points of attachment. It is not, however, with additional attractive forces, interesting and important as they are, that we must here concern ourselves.

The theoretical expression for the Arrhenius energy of activation in benzene solution is

$$E_A = E + 0.928E_e, \quad (24)$$

irrespective of the sign of  $E_e$ . The two series of experiments for which the results have been discussed in the last section indicate that  $E_e$  is

† *Trans. Chem. Soc.*, 829, (1935); 432, (1936).

positive. Comparison with the data for the Menschutkin reactions in benzene enables us to write

$$E_e = 3060\mu_A\mu_B \text{ (debyes)},$$

from which we see that  $E_e$  is always a significant fraction, and may even constitute most of the total energy of activation.

The most surprising feature of the investigation of reactions between polar molecules so far is, however, the fact that the electrostatic contribution to the energy of activation is positive, although, on chemical grounds, we have every reason to suppose that the reacting molecules align themselves in such positions that the interaction between the dipoles is negative. How this may come about is readily understood when we make allowance for the form of the intrinsic repulsion, which, as on p. 176, we shall take to be represented by the single term  $Aa^{-9}$ . The energy of the two molecules is then

$$u = Aa^{-9} - Ba^{-3}, \quad \text{VI (32)}$$

which can also be given in the entirely equivalent form†

$$u = \frac{|-u_0|}{2} \left\{ \left( \frac{a_0}{a} \right)^9 - 3 \left( \frac{a_0}{a} \right)^3 \right\}. \quad (25)$$

The terms  $a_0$  and  $u_0$  have been defined on p. 177. The expression for  $B$  is  $2\mu_A\mu_B(D+2)/3D$  (equation (34) of Chapter VI), so that we have

$$u = \frac{2\mu_A\mu_B}{3a_0^3} \left( \frac{D+2}{3D} \right) \left\{ \left( \frac{a_0}{a} \right)^9 - 3 \left( \frac{a_0}{a} \right)^3 \right\}. \quad (26)$$

Thus the energy of interaction between the dipoles, when taken in conjunction with the intrinsic repulsion, leads to a composite energy which may be positive or negative, but which is always proportional to  $\mu_A\mu_B$ . A plot for the particular system pyridine-methyl iodide in benzene solution is shown in Fig. 8 for which  $a = 2.24 \text{ \AA}$ . and  $-u_0 = 3,385 \text{ cals}$ . The minimum energy of the pyridine-*iso*-propyl iodide system is found to be  $= -5,320 \text{ cals}$ .

If we denote by  $a_c$  the distance apart of the dipoles in the reactive complex, we may write for the electrostatic contribution to the activation energy

$$\frac{E_e}{N_0} = u_c = \frac{|-u_0|}{2} \left\{ \left( \frac{a_0}{a_c} \right)^9 - 3 \left( \frac{a_0}{a_c} \right)^3 \right\}. \quad (27)$$

The experimental value of  $E_e$  has been shown to lie between 9,200

† See Lennard-Jones and Devonshire, *Proc. Roy. Soc., A*, **163**, 53, (1937); Moelwyn-Hughes, *Trans. Faraday Soc.*, **34**, 93, (1938).

and 12,700 calories. On solving for  $a_c$  we find it to be  $1.67 \pm 0.03 \text{ \AA}$ . At such short distances the use of the uncorrected dipole moments and of an attractive energy function of the form  $Ba^{-3}$  cannot be fully

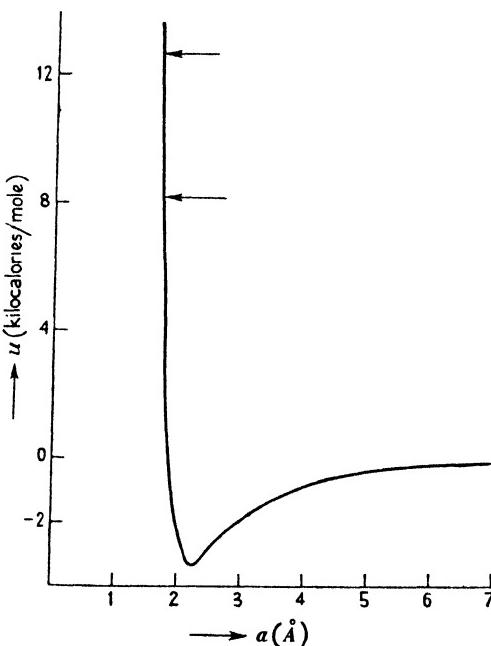


FIG. 8. The energy of interaction of pyridine and methyl iodide in benzene solution.

$$u = \frac{1.66 \times 10^{-62}}{a^9} - \frac{3.95 \times 10^{-36}}{a^3} \text{ ergs.}$$

justified, and the limitation, necessitated in any attempt to explain the problem with a minimum of mathematics, is one that should not be overlooked.

### *The Problem of Slow Reactions*

The adjective 'slow' is here applied in its relative sense, without reference to the absolute velocity of chemical change, to any bimolecular reaction for which the constant,  $A$ , of the integrated equation of Arrhenius

$$k = Ae^{-E_A/RT} \quad \text{I(4)}$$

is less than the lower limit of the range  $3 \times 10^{11 \pm 1}$ . The bimolecular velocity coefficients of the reaction between pyridine and ethyl iodide at decinormal concentrations in acetone solution, for example, are

found to be reproduced, over a range of some 40 degrees, by the equation†

$$k = 3.55 \times 10^6 \times e^{-14390/RT}.$$

The ratio of  $A/Z$  in this case is seen to be about  $10^{-6}$ . Smaller values are sometimes found (see Table III (2)).

Slow reactions of this type were first found in solution, and it was natural that the phase in which the reaction takes place should have been held responsible for their apparent anomalies. Christiansen,‡ as we have seen, suggested that deactivations of the reactive complex by solvent molecules could explain the effect, but the view was experimentally shown to be untenable.§ The rate of these reactions in the vapour phase, even allowing for considerable surface catalysis, is of the same order of magnitude as the rate in solution.

How the low value of the ratio  $A/Z$  is to be explained depends on whether  $E_A$ , which in this instance is 14,390 calories, is accepted as an apparent or as a true energy of activation. The former assumption, historically the first, is the more difficult to handle.

Discussions based on the latter assumption can be summarized by adding to the internal phase factor ( $p$ ) and the steric factor ( $s$ ) of Bradfield and Jones (p. 138) an additional factor ( $o$ ) to take account of the orientation of the reactant molecules with respect to each other and to the solvent molecules. We then have

$$k = psoZe^{-E_A/RT}, \quad (28)$$

from which, with the implied temperature invariance of all terms, it follows that

$$P = A/Z = pso. \quad (29)$$

One naturally hesitates before assigning numerical values to the complicated factors  $p$ ,  $s$ , and  $o$ . It has been argued|| that, in powers of  $10^{-1}$ , the following assignments are reasonable:  $p$  (2),  $s$  (1), and  $o$  (4–5), so that, with all the adverse effects acting jointly and in full swing, ' $P$  will be of the order of  $10^{-8}$ '. According to this view, molecules of pyridine and ethyl iodide possessing sufficient energy to ensure chemical change must collide about  $10^6$  times before effecting it. It is as if a person, possessing power enough to push a door open,

† Gibson, Fawcett, and Perrin, *Proc. Roy. Soc., A*, **150**, 223, (1935).

‡ *Z. physikal. Chem.*, **113**, 35, (1924).

§ Moelwyn-Hughes and Hinshelwood, *Trans. Chem. Soc.*, **230**, (1932).

|| Hinshelwood and Winkler, *ibid.*, 371, (1936). In this paper (footnote to p. 373) appears the only attempt, of which we are aware, at an explicit justification for identifying the true energy of activation with  $E_A$ . The implicit assumption is common.

should have to try to do so a million times before succeeding. His failure could quite naturally be ascribed to the intricacy of the latch, but it is worth while recalling that even in reactions of biological interest, where a very delicate mechanism of adjustment exists between the structure of enzyme and substrate, an inefficiency of this order of magnitude has not so far been encountered.

The other assumption is that  $E_A$  only indirectly reflects the energy of activation. An earlier statement† may here be cited:

'Considering the results of Table III (2) broadly, we see that the divergence between the experimental and theoretical  $k$ 's diminishes steadily as the observed value of  $E_A$  increases, finally disappearing as  $E_A$  approaches that quantity (21,000) which is characteristic of normal reactions proceeding with this rate. It would appear, therefore, that the observed critical increments given in this table are false, in the sense that —by some unknown mechanism—they have been depressed from the normal values. The problem thus resolves itself into tracing the cause for the low values not only of  $A$  (of the Arrhenius equation—I (4)) but also of  $E_A$ .'

The development of this idea demands a closer inspection of the mechanism of reaction, and a recognition of the dependence of the apparent energy of activation,  $E_A$ , on the temperature,  $T$ , the dielectric constant,  $D$ , the pressure,  $P$ , and the viscosity,  $\eta$ , for which, except in the last case, there is, in general, direct experimental proof.

#### *The Mechanism of Reaction between Polar Molecules in Solution*

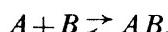
When polar molecules dissolve, the first interaction of which we take note is the formation of intermolecular complexes. This attitude is dictated by our knowledge of the cryoscopic, ebullioscopic, absorption, and photometric properties of solutions, as well as the distribution of solutes between different solvents (p. 174). There is no need to be vague about such complexes. In 10 litres of a benzene solution containing one gram molecule each of pyridine and *p*-chlorophenol, the fraction of molecules which has united into the complex state is 0.0113 at 25° C., and 0.114 at 100° C.

It has long been supposed that such complexes play an important role in the kinetics of reaction in solution. Energy changes associated with their formation offer a means of understanding how the solvent may exert an effect both specific and profound, and are comparable

† *Chem. Rev.* **10**, 260, (1932).

in magnitude with the observed variations in the apparent energies of activation.

The hypothesis, frequently formulated,<sup>†</sup> may be applied here to the specific case of the reaction between pyridine and ethyl iodide in acetone solution, which is a fairly representative example. We have, in the absence of direct data referring to the complex formed, to use a theoretical expression for the equilibrium constant  $K$ , covering the reaction



which is<sup>‡</sup>

$$K = \frac{n_{AB}}{n_A n_B} = \frac{N_0}{1000} \frac{r_1^2}{\nu} \left( \frac{8\pi kT}{m^*} \right)^{\frac{1}{2}} e^{-\Delta E/RT}, \quad (30)$$

where  $n_{AB}$  is the equilibrium concentration of complex, and  $n_A$  and  $n_B$  stand for the equilibrium concentrations of the unassociated solutes.  $r_1$  is the distance apart of the centres of gravity of the two molecules, and  $\nu$ , the intermolecular frequency, is given in terms of the distance,  $r_2$ , apart of the centres of the dipoles responsible for the attraction:

$$\nu = \frac{3}{2\pi r_2} \left( \frac{3| -u_0 |}{m^*} \right)^{\frac{1}{2}}. \quad VI (38)$$

The excess molar entropy of complex molecules at a concentration of one gram molecule per litre over the molar entropies of the unassociated molecules at the same concentration is then

$$\Delta S^0 = R \ln \left\{ \frac{N_0}{1000} \frac{2\pi r_1^2 r_2}{3} \left( \frac{8\pi kT}{3| -u_0 |} \right)^{\frac{1}{2}} \right\}. \quad (31)$$

The numerical values, according to equations I(17), VI(35), and VI(36), are  $r_1 = 6.3 \text{ \AA.}$ ,  $r_2 = 1.7 \text{ \AA.}$ , and  $-u_0 = 1,900$  calories per mole; hence

$$\Delta S^0 = -3.84 \text{ calories/gm. mol.-degree,}$$

which enables us to write

$$K = 0.145 \times e^{+1900/RT}.$$

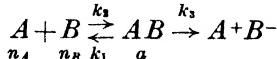
This complex has, according to the stationary state hypothesis, the choice of reverting into ordinary molecules or of passing over, with the acquisition of energy, into products.

Let it now be supposed that only those molecules which have

<sup>†</sup> *Ibid.*, 10, 230, (1932); *Trans. Chem. Soc.*, 101, (1936); *Acta Physicochim. U.S.S.R.*, 4, 173, (1938).

<sup>‡</sup> Equation (64) of Appendix I. Cf. Moelwyn-Hughes, *Physical Chemistry*, p. 507, Cambridge, (1940).

united into complexes undergo chemical change. We then have the scheme:



according to which the rate of chemical change is

$$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \left( \frac{k_2 k_3}{k_1 + k_3} \right) n_A n_B$$

and the observed bimolecular velocity coefficient is

$$k = \frac{k_2 k_3}{k_1 + k_3}. \quad (32)$$

If the complex is much more likely to react than to revert (i.e. if  $k_3 \gg k_1$ ), we conclude that  $k = k_2$ , which is the mechanistic equivalent to the assumption that  $E_A = E_2$ . If, on the other hand, the complex is much more likely to dissociate into its original components (i.e. if  $k_1 \gg k_3$ ), we conclude that

$$\begin{aligned} k &= k_3(k_2/k_1) \\ &= k_3 K \\ &= k_3 e^{\Delta S^\circ / R} e^{-\Delta E / RT}, \end{aligned} \quad (33)$$

from which it follows that, omitting the term  $(\frac{1}{2})RT$ ,

$$E_A = E_3 + \Delta E. \quad (34)$$

It has been shown that  $\Delta E$  is probably  $\sim 1.9$  kilocalories, hence the true energy of activation becomes

$$E_3 = E_A + 1.9.$$

The correction, though small, is in a direction which accounts for an apparent slowness. Previous passages in this chapter indicate that  $-\Delta E$  lies within the somewhat wide limits of  $1.9 \pm 5.9$ . We shall, however, merely adopt the smallest value, as we are interested in seeking to understand the problem and not in explaining it away.

The next correction to be considered arises from the fact that the collision formula, which is the standard upon which the alleged abnormality is gauged, refers to systems at constant volume, whereas the kinetic data refer to constant pressure. In the case of the reaction under review, the difference

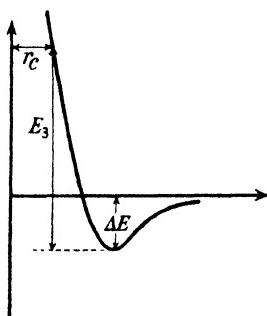


FIG. 9.

$E_V - E_P$  is known to be  $2.0 \pm 0.2$  kilocalories (p. 355), and it is important to note its sign. On adding, we have:

$$\begin{array}{rcl} E_A (\text{observed}) & 14.4 \pm 0.3 \\ E_P - E_V & 2.0 \pm 0.2 \\ -\Delta E & 1.9 \\ \hline & 18.3 \pm 0.5 \end{array}$$

A reaction with the velocity of the present one would be regarded as normal if the energy of activation were  $22.9 \pm 1.4$ . The two corrections considered thus reduce the factor  $P$  to  $10^{-3 \pm 1}$ .

The arguments advanced here are equally applicable to complexes formed between solute and solvent molecules, and it is, in fact, in terms of them that the present formulation has most frequently been given. There appears, however, to be no direct cryoscopic evidence in those cases which have been examined,† but their role cannot, for all that, be dismissed. Grimm, Ruf, and Wolff,‡ in particular, have discussed their bearing on the velocity of Menschutkin's reaction in mixed solvents composed of hydrocarbons and the four phenyl halides.

The part played by activated complexes may also be formulated in the same way. Here we are entitled to look for much larger energy and entropy terms. In equation (33), for example, we now let  $K$  refer to the equilibrium established between activated complex molecules and normal reactants, and replace the specific constant  $k_3$  by the general frequency term  $kT/h$  (equation (75), Appendix I), obtaining

$$k = \frac{kT}{h} e^{\Delta S_c/R} e^{-\Delta E_c/RT}. \quad (35)$$

This is essentially the step taken by Eyring and Wynne-Jones.§ We see that on this basis  $E_A = RT + \Delta E_c$ ,

$$\text{and that } \Delta S_c^0 = R \left\{ \ln \left( \frac{hA}{kT} \right) - 1 \right\}. \quad (36)$$

The numerical value of  $\Delta S_c^0$  for reactions which, at  $25^\circ \text{ C.}$ , have rates predicted by the collision theory, is obviously  $-8.10 \text{ cals./gm. mol.-deg.}$  From the data of Table 5,  $\Delta S_c^0$  is seen to vary from  $-37$  to  $-60$ ; the changes in molar entropy attending the formation of the corresponding quaternary ammonium salts (Table VI(3)) in different

† Cox, *Trans. Chem. Soc.*, **119**, 142, (1921).

‡ *Loc. cit.*

§ *J. Chem. Physics*, **3**, 492, (1935).

solvents vary from -22 to -57. This rather striking parallelism has been interpreted by Wynne-Jones and Eyring† as evidence that the critical complex closely resembles the actual product, and is therefore salt-like in structure. The supposition that a reactive complex differs from, or resembles the products of reaction, according as  $\Delta S_c^0$  differs from or lies near to  $\Delta S^0$ , may prove a very helpful one. It does not, it may be noted, in any way hinge on our acceptance of  $kT/h$  as the frequency of the unimolecular step denoted by  $k_3$ , but can be applied to any series of comparable reactions wherein it is justified to attribute a common value to the frequency term concerned.

Many earlier attempts at devising a kinetic analogue of the essentially thermodynamic function known as entropy have been made,‡ but it is only to one of these that we can here refer.

As each of the constants of equation (32) may, within narrow limits, be expressed in the form  $k = Ce^{S/R}e^{-E/RT}$ , where  $S$  denotes an entropy difference and  $E$  an energy difference, we see that we can rewrite it as follows:

$$k = k_2 \frac{C_3 e^{S_3/R} e^{-E_3/RT}}{C_1 e^{S_1/R} e^{-E_1/RT} + C_3 e^{S_3/R} e^{-E_3/RT}}. \quad (37)$$

Conditions may sometimes arise when the  $C$  and  $E$  factors so co-operate as to lead to a principal equation of the form

$$k = Ce^{-E/RT}e^{S_3/R}/(e^{S_1/R} + e^{S_3/R}). \quad (38)$$

The last fraction in this equation has been termed by Soper§ the 'breakdown' factor. Soper's derivation is based on general arguments concerning probabilities, which he has shown to be connected with the difference in polarity of the reactants and the complex|| and, in many cases, to run parallel with the kinetic abnormality.

The most important aspect of the work of Kohnstamm, Trautz, Soper, Wynne-Jones, and Eyring in this connexion is the evidence it affords for regarding as reasonable a resolution of the total entropy change attending a chemical reaction into separate entropy changes ascribable to the direct and reverse activations:

$$\Delta S = S_2 - S_1 = (S_c - S_1) - (S_c - S_2) = \Delta S_1 - \Delta S_2. \quad (39)$$

No formal justification can be given for the treatment, and certainly

† *Loc. cit.*

‡ Kohnstamm and Scheffer, *Verlag Akad. Wetensch. Amsterdam*, **19**, 878, (1911); Trautz, *Z. physikal. Chem.*, **68**, 637, (1910); *Z. Elektrochem.*, **25**, 4, (1915).

§ *Trans. Chem. Soc.*, 1393, (1935).

|| R. E. Roberts and Soper, *Proc. Roy. Soc., A*, **140**, 71, (1933).

no general agreement exists as to where the dividing line should be drawn, but like the kindred relations involving energies and volumes,

$$\Delta E = E_2 - E_1 = (E_c - E_1) - (E_c - E_2) = \Delta E_1 - \Delta E_2, \quad \text{I (38)}$$

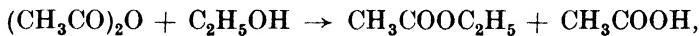
$$\Delta V = V_2 - V_1 = (V_c - V_1) - (V_c - V_2) = \Delta V_1 - \Delta V_2, \quad \text{XI (8)}$$

it may be vindicated *a posteriori*. Its bearing on the problem of slow reactions is, of course, to restate rather than to solve it.

### *An Alternative Explanation of apparently Slow Rates of Reactions*

It is possible that some reactions in solution which ostensibly take place between neutral molecules are in fact reactions between one neutral molecule and an ion formed by the dissociation of the other molecule.<sup>†</sup> The velocity would then appear to be slow because the number of ions is small compared with the number of molecules. To put the idea to the test we require a knowledge of dissociation constants, in various solvents and at different temperatures, which is seldom available.

The first quantitative application of this hypothesis was to the reaction



which has been shown<sup>‡</sup> to be a slow reaction. In two typically inert solvents the bimolecular velocity coefficients are

$$k_2 = 9.16 \times 10^4 \times e^{-12400/RT} \quad (\text{hexane})$$

and  $k_2 = 4.14 \times 10^5 \times e^{-13400/RT}$  (carbon tetrachloride).

The reaction has also been measured in ethylalcoholic solution,<sup>§</sup> under which conditions the rate—now naturally a pseudounimolecular one—is found to be given by the equation

$$k_1 = 5.87 \times 10^7 \times e^{-17550/RT}.$$

If the reaction takes place only between acetic anhydride molecules and the ethoxide ion, we have

$$\begin{aligned} k_2 &= - \frac{d[(\text{CH}_3\text{CO})_2\text{O}]}{dt} \frac{1}{[(\text{CH}_3\text{CO})_2\text{O}][\text{C}_2\text{H}_5\text{O}^-]} \\ &= k_1 / [\text{C}_2\text{H}_5\text{O}^-] \\ &= k_1 K^{-1}, \end{aligned}$$

where  $K = [\text{C}_2\text{H}_5\text{O}^-][\text{H}^+]$ .

<sup>†</sup> Brühl, *Berichte*, **32**, 2326, (1899); Euler, *Z. physikal. Chem.*, **32**, 348, (1900).

<sup>‡</sup> *Trans. Chem. Soc.*, 230, (1932).

<sup>§</sup> Moelwyn-Hughes and Rolfe, *ibid.*, 241, (1932); Williams, Perrin, and Gibson, *Proc. Roy. Soc., A*, **154**, 684, (1936).

In this particular instance electromotive and thermal data are available† which can be combined to give the ionic concentration at various temperatures:

$$K^{\ddagger} = 8.1 \times 10^{-6} \times e^{-5820/RT}.$$

On combining the kinetic with the static information we have

$$k_2 = 7.2 \times 10^{12} \times e^{-11730/RT}.$$

The rate of reaction, superficially regarded as slow, is thus actually somewhat greater than can be accounted for by assuming that each activating collision between the acetic anhydride molecule and the ethoxide ion is effective. The same conclusion is reached if we examine the possibility that the rate is influenced by collisions between solute and solvent molecules. Experimentally, we then have

$$k_1/\eta = 1.26 \times 10^{12} \times e^{-20800/RT}.$$

The theoretical value of the pre-exponential term is  $1.4 \times 10^{11}$ .

How far the ionization hypothesis can extend to other reactions, or, in fact, to this reaction in other solvents, cannot be judged until more extensive thermodynamic constants are measured. In the meantime we must guard against the danger of assuming that a molecule in solution is un-ionized simply because we do not happen to have measured its ionization constant.

The reverse operation has sometimes been tried. The ionization constant of a sparingly ionized solute may be computed by assuming that the rate of reaction attributed to the parent molecule is in fact due to an ion produced by it. The degree of ionization of methyl iodide in nitrobenzene solution would thus appear to have the order of magnitude  $10^{-20}$ .‡

### *Quantal Considerations*

There is no reason why a molecule, possessing sufficient energy, should not find it easier to react with a second molecule than with a third one, or why two molecules should not find one solvent medium more conducive to union than another. Low values of  $P$  may, in short, be real; and we have been at pains in this chapter to discover whether what appears to be a high inefficiency of activating collisions is genuine, or whether it arises from our failure to disentangle the

† Macfarlane and H. Hartley, *Phil. Mag.*, **13**, 425, (1932).

‡ *Acta Physicochim. U.S.S.R.*, **4**, 201, (1936).

various factors which are comprehensively referred to as solvent effects. When we reflect on the formulation of kinetic expressions in terms of the quantum theory (Appendix I), we shall see that the term  $P$  may be accurately evaluated in very simple cases, such as triatomic reactions in the gaseous phase. Approximate calculations may also be made relating to reactions between complicated molecules, as has been frequently shown.† A searching theoretical treatment of the problem of slow reactions, on the basis of both classical and quantal mechanics, has been given by Hellmann and Syrkin.‡

† e.g. by Bawn, *Trans. Faraday Soc.*, **31**, 1536, (1935) and by Benford and Wassermann, *Trans. Chem. Soc.*, 367, (1939).

‡ *Acta Physicochim. U.S.S.R.*, **4**, 433, (1935).

## VIII

### THE FREQUENCY OF MOLECULAR COLLISIONS

WE have progressed so far by applying to a variety of problems only two collision formulae. One would, in fact, have taken us quite a long way, but an early introduction of the second equation seemed desirable in order to stress the distinction between the type of collision suffered by two molecules of solute and that suffered by one molecule each of solute and solvent. The numbers of such collisions taking place in unit time and in unit volume of solution are, respectively,

$$_A Z_B = n_A n_B (r_A + r_B)^2 \left[ 8\pi k T \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{\frac{1}{2}} \quad I(21)$$

and  $_A Z_S = 3\pi\eta n_A r_A / m_A.$  I (28)

Here  $n$ ,  $r$ , and  $m$  stand for the molecular concentration, radius, and mass, and  $\eta$  for the viscosity of the solvent (subscript  $S$ ) at a temperature,  $T$ . A third collision formula, somewhat intermediate in type, applies to collisions of the solute-solvent type wherein a second molecule of solute is also present, and when one of the solutes is comparable to the solvent. It gives for the frequency of binary collisions

$$_A Z_B = \frac{3\pi\eta}{4} \frac{n_A n_B}{n_S} (r_A + r_B) \left( \frac{1}{m_A} + \frac{1}{m_B} \right). \quad I(30)$$

We have thus two expressions for the frequency of binary collisions in solution, one of which is independent of, and the other directly proportional to, the viscosity. Other formulae, to be discussed later, share with these three the obvious limitations inherent in the oversimplification of the models which have made their derivation at all possible. Equation I(21) in particular is based on the impossible assumptions of sphericity, impenetrability, and absence of attractive forces. The problem we have to face, however, is not whether this formula is accurate for gaseous systems, but whether, crude though it is, it represents correctly as regards order of magnitude the frequency of binary collisions between solute molecules. This is an intricate problem about which, happily, experiment has something to say; and it is with relief that we turn from the pitfalls of theoretical conjectures to the firm ground of fact.

If bimolecular reactions, which by definition depend on the fre-

quency of binary collisions, were to be found to proceed with the same velocity in the gaseous state as in solution, we would, unless we were particularly looking for trouble, assume the energy of activation and the collision frequency to be both unaffected by the presence of the solvent. A ratio of the velocities in the two phases differing markedly from unity would, on the other hand, indicate, in sign and magnitude, new environmental effects. This method of approaching the problem is, in principle, extremely simple.

### *A Comparison of Bimolecular Reactions in the Gaseous Phase and in Solution*

Chlorine monoxide decomposes in the gaseous phase by a mechanism which has been variously interpreted as indicating consecutive bimolecular reactions,<sup>†</sup> straight<sup>‡</sup> and branched chains.<sup>§</sup> For our purpose the precise mechanism is immaterial. In carbon tetrachloride solution, chlorine monoxide decomposes by the same mechanism, and with the same velocity, as in the gas phase.<sup>||</sup> In Table 1,  $t_{20-60}$  per cent. represents the time required by the reaction to proceed from 20 per cent. to 60 per cent. of completion. Within the limits of experimental uncertainty the rate of decomposition in solution equals that in the

*Table 1*

$[Cl_2O]$ (gram molecule per litre)	$t^\circ C.$	$t_{20-60}$ per cent. (minutes)		$\frac{t_{\text{solution}}}{t_{\text{gas}}}$
		For solution	For gas	
0.224	70.7	50	47.5	1.05
0.115	71.0	105	90.5	1.16
0.115	59.8	257	225	1.14
0.126	69.8	83	90.5	0.92
0.095	69.7	100	122	0.82
0.120	80.1	55	44	1.25
0.120	75.3	54	61	0.89
0.120	65.2	139	137	1.02
0.120	60.1	200	211	0.95

gas, the ratio  $t_{\text{solution}}/t_{\text{gas}}$  having an average value of 1.02. The energy of activation for the reaction in solution is  $20.3 \pm 0.5$  kilocalories, and for the reaction in the gas phase is about 21.0 kilocalories.

<sup>†</sup> Hinshelwood and Prichard, *Trans. Chem. Soc.*, 2730, (1923).

<sup>‡</sup> Beaver and Stieger, *Z. physikal. Chem.*, B, 12, 93, (1930).

<sup>§</sup> Semenoff, *Chemical Kinetics and Chain Reactions*, p. 385, Oxford, (1935).

<sup>||</sup> Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, A, 131, 177, (1931).

The chlorine-sensitized decomposition of ozone in the gaseous phase follows the law

$$-\frac{d[\text{O}_3]}{dt} = k[\text{Cl}_2]^{\frac{1}{2}}[\text{O}_3]^{\frac{1}{2}} \quad \text{or} \quad k = \frac{1}{(t_2 - t_1)[\text{Cl}_2]^{\frac{1}{2}}} \left( \frac{1}{[\text{O}_3]_{\frac{1}{2}}} - \frac{1}{[\text{O}_3]_{\frac{1}{2}}} \right),$$

which is best explained in terms of a chain mechanism.† In carbon tetrachloride solution, where the velocity of the uncatalysed reaction cannot be neglected, a plausible rate equation is

$$-\frac{d[\text{O}_3]}{dt} = k[\text{Cl}_2]^{\frac{1}{2}}[\text{O}_3]^{\frac{1}{2}} + k_1[\text{O}_3]$$

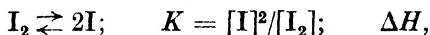
or  $k_1 t = \ln \frac{[\text{O}_3]_0}{[\text{O}_3]_t} - 2 \ln \left( \frac{k[\text{O}_3]_0^{\frac{1}{2}}[\text{Cl}_2]^{\frac{1}{2}} + k_1}{k[\text{O}_3]_t^{\frac{1}{2}}[\text{Cl}_2]^{\frac{1}{2}} + k_1} \right).$

The data found for the reaction in solution‡ conform moderately well with this equation, giving, at 50° C., an average value of  $k$  equal to  $1.45 \times 10^{-2}$  litres per mole-second. Comparison with the value of  $9.50 \times 10^{-3}$  found by Bodenstein, Padelt, and Schumacher for the gas reaction gives us  $k_{\text{solution}}/k_{\text{gas}} = 1.53$ . The two values of  $E_A$  also differ somewhat.

The rate of decomposition of ethylene iodide in carbon tetrachloride solution can be represented by the relation§

$$+\frac{d[\text{I}_2]}{dt} = k[\text{C}_2\text{H}_4\text{I}_2][\text{I}_2]^{\frac{1}{2}}; \quad E_A,$$

which is consistent with the rapid maintenance of the equilibrium



followed by the measurable process



Hence (cf. p. 51),  $k_2 = kK^{-\frac{1}{2}}$  and  $(E_A)_2 = E_A - \frac{1}{2}\Delta H$ .  $(E_A)_2$  is found to be 29,900 calories. The same reaction has been studied in the gas phase, with allowance for a concurrent spontaneous decomposition

$$+\frac{d[\text{I}_2]}{dt} = k[\text{C}_2\text{H}_4\text{I}_2][\text{I}] + k_1[\text{C}_2\text{H}_4\text{I}_2].$$

$(E_A)_2$  has now the value 30,200 calories.|| Compared at a common temperature the rates of the bimolecular reaction in the two phases

† Bodenstein, Padelt, and Schumacher, *Z. physikal. Chem.*, **B**, *5*, 209, (1929).

‡ Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc.*, **A**, *134*, 211, (1931).

§ Polissar, *J. Amer. Chem. Soc.*, *52*, 956, (1930).

|| Arnold and Kistiakowsky, *J. Chem. Physics*, *1*, 166, (1933); Cuthbertson and Kistiakowsky, *ibid.*, *3*, 631, (1935).

differ by a factor of not more than 2. Within the limits imposed by experiment, the solvent is without influence on the kinetics of the reaction.

An example of unusual interest is the conversion of *para*- into *ortho*-hydrogen.<sup>†</sup> The extremely slow uncatalysed change is hastened by substances possessing a magnetic moment. With oxygen molecules, for example, we have a relatively fast reaction

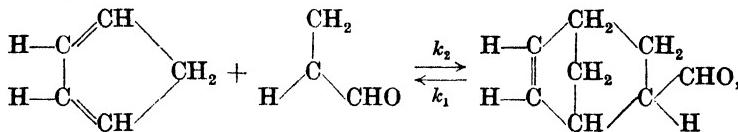


for which Farkas and Sachsse find

$$-\frac{d[p\text{-H}_2]}{dt} = k[p\text{-H}_2][\text{O}_2].$$

At 20° C., the catalytic coefficient in the gaseous phase is 9.16 and in aqueous solution is 10.5 litres/gram mole-second. Similar results have been found<sup>‡</sup> with nitric oxide, the catalytic coefficient for which, at the same temperature, is 0.442 litres/gram mole-second in water, and 0.453 times this value in the gaseous phase.

The addition of acraldehyde to *cyclo*-pentadiene is a reversible reaction,



for which the following expressions hold<sup>§</sup> in the homogeneous gas phase:

$$k_2 = 1.50 \times 10^6 \times e^{-15200/RT},$$

$$k_1 = 2.2 \times 10^{12} \times e^{-33600/RT}.$$

The bimolecular reaction, studied in benzene solution at temperatures about 150° C. lower,<sup>||</sup> yields the following results:

$$k_2 = 1.3 \times 10^6 \times e^{-13700/RT}.$$

The difference in the two  $(E_A)_2$  values is not greater than the experimental error.

The conversion of *cyclo*-pentadiene into dicyclopentadiene is a

<sup>†</sup> L. Farkas and Sachsse, *Z. physikal. Chem.*, **B**, **23**, 1, (1933); A. Farkas, *Ortho-hydrogen, Parahydrogen, and Heavy Hydrogen*, p. 83, Cambridge, (1935).

<sup>‡</sup> L. Farkas and Sandler, *Trans. Faraday Soc.*, **35**, 337, (1939); L. Farkas and Garbatski, *ibid.*, **35**, 263, (1939).

<sup>§</sup> Kistiakowsky and Lacher, *J. Amer. Chem. Soc.*, **58**, 123, (1936).

<sup>||</sup> Wassermann, *Trans. Chem. Soc.*, 1027, (1936).

homogeneous bimolecular reaction in the gaseous phase† and in a variety of solvents.‡ Kaufmann and Wassermann's data are summarized in Table 2, omitting only the case of acetic acid, with which, as the drift in the 'constants' show, there are complications. In these very varied conditions the term  $A$  is seen to lie within the remarkably narrow range of  $(2.5 \pm 2.0) \times 10^6$ .

*Table 2*  
*Bimolecular Velocity Constants (litres/gm. mol.-sec.) for  
the Association of Cyclo-pentadiene*

Medium	$k_{298.1} K \times 10^7$	$\log_{10} A$	$E_A$ (kilocalcs.)
Vapour	6.9	6.1	16.7
$C_6H_6$	6.6	6.1	16.4
$CCl_4$	7.9	6.7	17.1
$CS_2$	9.3	6.2	16.9
$C_6H_5NO_2$	13	5.5	15.1
$C_6H_5OH$	19	6.4	16.4

Under the catalytic influence of sodium atoms, the polymerization of butadiene is a relatively rapid reaction, the primary step in which consists of a bimolecular collision between the alkali atom and the organic molecule. In both the liquid and gaseous phases the velocity constant is  $k_2 = 4.7 \times 10^3 \times \exp(-7300/RT)$ .§

The kinetics of the formation of tetraethylammonium iodide and of the esterification of acetic anhydride by ethyl alcohol have also been investigated in the gaseous phase and in hexane and carbon tetrachloride solutions.|| The reactions in the gaseous phase, in spite of surface catalysis, proceed at rates which are of the same low order of magnitude as those in solution. These experiments prove that the apparent inefficiency (i.e. low values of  $P$ ) of slow reactions in solution is also an inherent one, which cannot be due, as had once been supposed, to deactivations by the solvent molecules. Due to the incidence, and possibly even the preponderance, of a heterogeneous mechanism in the 'gaseous' phase, they cannot yield precise information as to collision frequencies in the various systems. Similar results have later been found†† in the case of the union of triethylamine with methyl iodide in the gaseous phase, with and without added vapours.

† Kistiakowsky and Mears, *J. Chem. Physics*, **5**, 687, (1937).

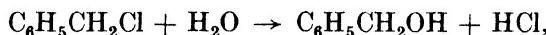
‡ Kaufmann and Wassermann, *Trans. Chem. Soc.*, 870, (1939).

§ Abkin and Medvedev, *Trans. Faraday Soc.*, **32**, 286, (1936).

|| Moelwyn-Hughes and Hinshelwood, *Trans. Chem. Soc.*, 230, (1932).

†† Gladishev and Syrkin, *Acta Physicochim. U.S.S.R.*, **8**, 323, (1938).

Esters, as it is well known, may be hydrolysed in water and distilled in steam. In other words, they react with water but not with water vapour. For example, the following reactions, which proceed smoothly in water below its boiling-point, do not take place to any measurable extent† during long hours at 200° C.,



Reactions in solution, therefore, may reveal features for which there is no parallel in gaseous systems. The distinction, when it appears, seems to be a genuine one, and not to be attributed to the relatively low molecular concentrations of the gaseous phase. Thus, for example, propylene and hydrogen chloride at 105° C. and at a pressure of 105 atmospheres do not react to any measurable extent in the gaseous phase in a time interval sufficient for complete reaction in the liquid phase.‡ It therefore becomes necessary to establish some standard velocity, not only for reactions which cannot be measured in the gas phase, but for those which do not occur in it.

### *Discussion*

'Since equation I (21) accounts for the rates of bimolecular gaseous reactions, it is to be concluded that it gives also a true value of the number of collisions between dissolved molecules in simple cases.'§ 'Considering the uncertainties of the extrapolation, we may conclude that the reaction velocity in solution and in the gas phase are essentially the same, and that the solvent has very little influence, not only on the activation energy, but also on the collision frequency between the reacting molecules.'|| 'It follows that the collision frequency in solution is of the same order of magnitude as that in the gas phase, not only for normal bimolecular reactions, but also for a reaction of the slow type.'†† 'We are necessarily led to the conclusion that  $Z_{\text{gas}}$  and  $Z_{\text{solution}}$  are approximately equal.'‡‡ 'It can be concluded that the collision number in polar solvents, in non-polar solvents, and in the gas phase is of the same order of magnitude.'§§

These quotations summarize an important experimental conclusion

† Harker, *Trans. Chem. Soc.*, 500. (1924); Miyamoto, *Bull. Chem. Soc. Japan*, 9, 501, (1934).

‡ H. S. Sutherland and Maass, *Canadian Journal of Research*, 5, 48, (1931).

§ Moelwyn-Hughes, (1932).

|| Arnold and Kistiakowsky, (1933).

†† Wassermann, (1936).

‡‡ Farkas and Garbatski, (1939).

§§ Kaufmann and Wassermann, (1939).

from which no one acquainted at first hand with the measurement of reaction velocity in the two systems dissents.

According to equation I (21), the ratio of the binary collision frequencies in dilute solution and in the gaseous phase is, of course, unity. If, however, we are interested in binary collisions taking place in the presence of a third particle, we obtain, from equation I (30), the ratio

$$\frac{{}_A Z_B \text{ (solution)}}{{}_A Z_B \text{ (gas)}} = \left( \frac{\eta_s}{\eta_g} \right) \left( \frac{n_g}{n_s} \right). \quad (1)$$

This again is obviously unity under the only conditions which make the comparison legitimate, i.e. those wherein the molecular concentrations of the diluent in the two phases are equal. It is worth noting, however, that, due to the compensating effects of density and viscosity, a ratio approximating to unity may prevail under conditions far removed from the critical one.

On comparing the observed velocities with those reproduced by equation I (21), using the most exacting method (p. 69), we find the kinetic value of the sum of the radii,  $r_A + r_B$ , to be  $2.0 \text{ \AA}$ . for the chlorine monoxide and  $2.1 \text{ \AA}$ . for the ethylene iodide reaction. This equation therefore, despite its artificiality and other shortcomings, is not at all a bad one to have adopted as a basis for the general study of the velocity of chemical reactions in both the dissolved and the gaseous states of matter.

### *Other Collision Formulae*

Varied and numerous attempts have been made in recent years to evaluate the frequency of collisions in solution.

The mathematical theory of the coagulation of collosols† forms the basis of many treatments. According to this theory, the number of spherical particles of type *A*, the centres of which diffuse in time *dt* to within a distance ( $r_A + r_B$ ) of the centre of a spherical molecule of type *B*, is given in terms of the coefficient of diffusion, *D*, by the expression

$$4\pi D_A n_A (r_A + r_B) \left[ 1 + \frac{r_A + r_B}{(\pi D t)^{1/2}} \right] dt.$$

In order to find the total number of collisions made in unit time between all particles of type *A* and all particles of type *B*, we multiply this expression by  $n_B$ , add a similar product obtained by

† Smoluchowski, *Z. physikal. Chem.*, **92**, 129, (1918).

viewing the problem from the complementary angle, and divide the sum by 2 so as to avoid a double count. We then obtain

$${}_A Z_B = 2\pi(D_A + D_B)n_A n_B(r_A + r_B) \left[ 1 + \frac{r_A + r_B}{(\pi D_{A,B} t)^{\frac{1}{2}}} \right], \quad (2)$$

where

$$D_{A,B}^{\frac{1}{2}} = \frac{D_A + D_B}{D_A^{\frac{1}{2}} + D_B^{\frac{1}{2}}}$$

Conditions may arise when either of the terms in the brackets governs the behaviour of the system. When the first term dominates the situation, the number of collisions per unit volume is proportional to the time; when the second term dominates, this number is proportional to the square root of the time. Omission of the second term as negligible corresponds to the inequality

$$t \gg (r_A + r_B)^2 / \pi D_{A,B}.$$

The numerical value of the term on the right-hand side varies from about  $10^{-11}$  second for small molecules in water to about  $10^{-5}$  second for massive molecules, such as edestin, in the same solvent. It is, therefore, chiefly in colloidal solution that we look for examples of the square root law. Schütz† found that, at high substrate concentration, the extent of catalytic change by an enzyme is often proportional to the square root of the time. His law, which is found to hold for a wide variety of enzymic reactions, has been interpreted in terms of the theory of diffusion,‡ though numerous other interpretations, no less valid, are available.§ The rate of formation of Liesegang rings from colloidal solutions also obeys the square root law, and has been explained on the basis of the same theory.||

### 1. The Equation of Ölander

On combining equation (2) with the following expression†† for the coefficient of diffusion

$$D = kT/6\pi\eta r, \quad (3)$$

† *Z. physiol. Chem.*, **30**, 1, (1900).

‡ *Ergebnisse der Enzymforschung*, **6**, 23, (1937).

§ Arrhenius, *Immunochemistry*, 1st ed., p. 53, Leipzig, (1907); Langmuir, *J. Amer. Chem. Soc.*, **38**, 2221, (1916); Northrop, *J. General Physiol.*, **6**, 723, (1923); Euler, *Chemie der Enzyme*, 3rd ed., vol. i, p. 154, Munich, (1925); Moolwyn-Hughes, Pace, and Lewis, *J. General Physiol.*, **13**, 323, (1930).

|| Bauer, *Z. physikal. Chem.*, **B**, **27**, 145, (1934).

†† Einstein, *Ann. Physik*, **17**, 549, (1905); **19**, 289, (1906), whose derivation is given on p. 366. According to Cunningham (*Proc. Roy. Soc., A*, **83**, 357, (1910); see also Roughton, *ibid.*, **B**, **111**, 1, (1932)), the denominator must be multiplied by a numerical factor, which is a function of the radius and the average distance apart of the centres.

we obtain, after omitting the second term,

$$_A Z_B = \frac{kT}{3\eta} n_A n_B \frac{(r_A + r_B)^2}{r_A r_B}. \quad (4)$$

When multiplied by the factor  $\frac{1}{2}\pi$ , this expression is identical with a collision formula developed by Ölander.<sup>†</sup> Bradley<sup>‡</sup> has argued that the first term in Smoluchowski's equation is too large by a factor of 12, and has consequently proposed the equation

$$_A Z_B = \frac{1}{12}\pi(D_A + D_B)n_A n_B(r_A + r_B). \quad (5)$$

Ölander has applied equation (4) to certain reactions in aqueous solution, such as the inversion of cane sugar, and Bradley has examined most of the data of Table III (1) in the light of equation (5). The average value of  $(r_A + r_B)$  required to make things fit is the very reasonable one of 3.7 Å. in the case of some score of reactions between ions and polar molecules which, according to the simple collision theory, proceed with normal rates. As far as ability to reproduce the velocity at a given temperature is concerned, equation (5), is thus a satisfactory one, provided the inclusion of the factor 1/12 can be justified. The Ölander-Bradley theory of bimolecular reactions, however, is not so felicitous in other directions.

In the first place, it requires that the rate of reaction at a given temperature shall be inversely proportional to the viscosity, whereas, as far as we have been able to interpret the effects of high pressures, the velocity seems to be directly proportional to the viscosity. If a functional relationship of the form  $k = C\eta^\nu$  be used, then  $\nu$  is found to have positive values from 0.4 to 2.0, but never a negative value, though such a result is not excluded from the realm of possibility (equation VII (18)). Even in the apparently anomalous case of the inversion of cane sugar,  $\nu$  can be shown to be positive. At 15° C. a pressure of 500 atmospheres decreases the velocity by 6 per cent. and the viscosity by 3 per cent. On analysing the complete data we find that  $\nu$  may here have any value from 0.1 to 2.0. The effect of pressure on all bimolecular reactions hitherto examined is therefore to alter the velocity of reaction and the viscosity of the medium in the same direction, which indicates a direct, rather than an inverse, relationship between them.

In the second place, according to the Ölander-Bradley formulae,

<sup>†</sup> *Z. physikal. Chem.*, **144**, 118, (1929).

<sup>‡</sup> *Trans. Chem. Soc.*, 1910, (1934).

which, as we have seen, differ only by a numerical factor, the ratio of the rates of reaction in the gas phase and in solution should equal the inverse ratio of the viscosities of the media. Numerical calculations† give computed ratios of the order of magnitude of  $10^{-3}$ , which is not in agreement with experiment.‡

## 2. The Equation of Evans and Polanyi

According to equations (40) and (63) of Chapter VI, the equilibrium constant,  $K_s$ , for a reaction  $A + B \rightleftharpoons C$  in solution is related in terms of the solubilities,  $s$ , of reactants and products to the equilibrium constant,  $K_g$ , in the gas phase:

$$K_s = K_g \left( \frac{s_C}{s_A s_B} \right), \quad (6)$$

where

$$s = c_s/c_g. \quad (7)$$

Evans and Polanyi§ have argued that because  $K$  is proportional to the collision frequency,  $Z$ , and because  $s$  is proportional to  $e^{\Delta S^\circ/R}$ , where  $\Delta S^\circ$  is the excess of the molar entropy of the solute over that of the gaseous reactant, we may write

$$\frac{Z_s}{Z_g} = \frac{e^{\Delta S^\circ \delta / R}}{e^{(\Delta S_A^\circ + \Delta S_B^\circ)/R}}, \quad (8)$$

according to which collision frequencies in general may be expected to vary with the nature of the solvent. The experimental fact that the ratio  $Z_s/Z_g$  is approximately unity for the reactions hitherto examined is then regarded as evidence that the sum of the standard entropy changes suffered by the reactants on dissolving equals that which would be suffered by the reactive complex on dissolution. As a rule, however, the transition state theory leads to values of  $Z_s/Z_g$  which exceed unity by two to three powers of ten, and to collision frequencies in solution which are explicitly stated to be uninfluenced by the viscosity.

## 3. The Equation of Bradley

On account of the structural similarity of liquids and solids, particularly in the neighbourhood of the melting-point, we may imagine a molecule in a liquid at low temperatures to be, for the most part, hemmed in by its neighbours, which are, say,  $c$  in number.

† *Acta Physicochim. U.S.S.R.*, **4**, 185, (1936).

‡ Another criticism of Ölander's theory put forward in the first edition of this work (p. 119) has been rightly shown by Bradley (*loc. cit.*) to be invalid.

§ *Trans. Faraday Soc.*, **31**, 875, (1935); **32**, 1333, (1936).

Translatory motion within a force-free cell resembles a to-and-fro motion, i.e. a vibration, about an average position and it is not difficult to estimate the frequency of such a vibration.

Let it be supposed that two neighbouring molecules, though kept on an average at a central distance  $a$  apart, are nevertheless capable of approaching each other more closely, so that their centres are separated by a distance of  $a_0$  only. The latitude of motion in one dimension is thus  $2(a-a_0)$ , and the motion repeats itself when the centre of gravity has passed through double this distance. If  $u$  is the average velocity of the molecule, then the frequency,  $\nu$ , of vibration is clearly  $u/4(a-a_0)$ . Now it is readily proved that the average velocity of a molecule of mass  $m$  in one dimension (not in one direction) is  $(2kT/\pi m)^{\frac{1}{2}}$ ; hence

$$\nu = \frac{1}{2(a-a_0)} \sqrt{\frac{kT}{2\pi m}}. \quad (9)$$

As a sufficiently good working proposition we may take it that during the execution of a complete linear vibration the vibrating molecule contacts one-third of those molecules which encase it. The number of solute-solvent collisions made per second by one molecule of solute is thus

$$_1Z_s = \frac{c}{6(a-a_0)} \sqrt{\frac{kT}{2\pi m}}. \quad (10)$$

This very interesting way of regarding collisions in liquids has been found helpful in dealing with a variety of problems, especially viscosity.<sup>†</sup> Its application to the kinetics of reactions in solution was, however, made much earlier by Lamble and W. C. McC. Lewis,<sup>‡</sup> who, in a study of the catalysed hydrolysis of methyl acetate, estimated that the hydrogen ion vibrated about its mean position with a frequency lying within the limits  $(1.5 \pm 1.2) \times 10^{14}$  seconds<sup>-1</sup>. Bradley<sup>§</sup> has developed the idea systematically, obtaining an equation which becomes identical with equation (10) when we replace the coordination number,  $c$ , by  $3^{\frac{1}{2}}\pi$ , which is 16.3. If this be the true mechanism of vibration in liquids, we conclude, by comparing its consequences with those of equation I(28), that the viscosity must be reproduced by the relation

$$\eta = \frac{(2\pi mkT)^{\frac{1}{2}}}{6\pi^2 a(a-a_0)}. \quad (11)$$

<sup>†</sup> See Andrade, *Phil. Mag.*, **17**, 497, (1934); Frenkel, *Acta Physicochim. U.S.S.R.*, **3**, 633, (1935).

<sup>‡</sup> *Trans. Chem. Soc.*, **105**, 2330, (1914).

<sup>§</sup> *Ibid.*, 1910, (1935).

Bradley has applied his formula in an interesting manner to the theory of diffusion in liquids, into details of which we cannot here enter, and to the problem of unimolecular reactions in solution, to which some reference is made in Chapter IX.

In order to evaluate the amplitude it is assumed that the average distance apart of two molecules in a liquid at constant pressure is linearly related to the absolute temperature:

$$a = a_0(1 + bT), \quad (12)$$

so that  $b$  may be found from the coefficient of linear expansion. Values of  $(a - a_0)$  so obtained are in agreement with those given by (11), and lead to vibration frequencies of the correct order of magnitude.

#### 4. The Equation of Wheeler

In a theory of liquids developed and extensively applied by T. S. Wheeler† the distance  $a$  is taken as a temperature variable ‘diameter’, derivable from the density of the liquid by means of equation 1(17), which assumes a hexagonal close-packing of the molecules. Many of the familiar properties of simple liquids are then found to be directly related to a function  $\beta$ , defined as follows:

$$\beta = \frac{2(a - a_0)}{a}. \quad (13)$$

The coefficient of cubical expansion,  $\alpha$ , the viscosity,  $\eta$ , and the vibration frequency,  $\nu$ , for example, become

$$\alpha = 3\beta/T, \quad (14)$$

$$\eta = \frac{8}{3\pi} \frac{(\pi m k T)^{\frac{1}{2}}}{\beta a^2}, \quad (15)$$

and

$$\nu = \frac{1}{\beta a} \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}}. \quad (16)$$

Following the same arguments as those which led to equations (28) and (30) of Chapter I, the frequencies of solute-solvent and of solute-solute collisions are then taken to be:

$$_1 Z_s = 2\nu \quad (17)$$

$$\text{and } {}_A Z_B = (\nu_A + \nu_B) \frac{n_A n_B}{n_S}. \quad (18)$$

The detailed application of these formulae to kinetic results‡ shows

† *Trans. Nat. Inst. of Sciences, India*, **1**, 333, (1938).

‡ Bradley, *loc. cit.*; Wheeler, *Proc. Indian Acad. Sciences*, **4**, 291, (1936); K. S. G. Doss, *ibid.*, **4**, 23, (1936).

that the latter equation leads to calculated rates of bimolecular reactions which are somewhat lower than those afforded by equation I (21), and that the introduction of one internal degree of freedom can adjust matters satisfactorily. Because, according to the present theory, the frequency of vibration is not quite so sensitive to temperature as is implied in equation I (28), the correction to the Arrhenius energy of activation,  $E_A$ , is not so great, and consequently the values of  $F$  needed to account for the rate of reactions in solution are lower by 1 or 2.

It need hardly be pointed out that the intensive search for improved collision formulae, applicable to the kinetics of reactions in solution, has had a stimulating effect on the theoretical study of the pure liquid state.

#### *On the Nature of the Variation in the Types of Collisions*

The two simple formulae which have been chiefly used in this work emphasize, though imperfectly, the distinction between two types of collisions. The frequency,  $Z$ , of collisions between one solute molecule and other solute molecules is proportional to the concentration. The frequency,  $Z$ , of collisions between one solute molecule and solvent molecules is independent of the concentration. These extreme types of collisions pertain chiefly to the gaseous and the solid states, and we must expect in solutions and in pure liquids to meet with an intermediate type, and with conditions of temperature and concentration wherein one kind of collision gradually changes into the other kind.

The relation between the two types may be derived as follows. We define the collision number in terms of the average velocity and the mean free path

$$Z = \frac{v}{\lambda}, \quad \text{I (23)}$$

and proceed to determine quantal forms for  $v$  and  $\lambda$  from which classical forms emerge as special cases.

According to the classical treatment of gases, the path,  $l$ , along which a gaseous molecule can travel is imagined to vary from zero to infinity. According to the quantum theory, the molecule, even at the absolute zero of temperature, retains a certain latitude of motion, within which it is guaranteed not to meet another molecule. This distance, which we shall denote by  $Q$ , may be taken as twice the

average displacement of a linear oscillator, and thus to have the value†

$$Q = \frac{1}{\pi} \left( \frac{\hbar}{\pi m v} \right)^{\frac{1}{2}}. \quad (19)$$

The probability that a molecule shall travel a path of length  $l$  unhindered is known to be

$$f(l) = e^{-Kl} + \text{a constant}. \quad (20)$$

We may set this probability as unity when  $l$  equals  $Q$ , so that the integration constant is  $1 - e^{-KQ}$ , and consequently

$$f(l) = e^{-Kl} + 1 - e^{-KQ}. \quad (21)$$

By differentiation, the probability that the molecule shall travel a distance  $dl$  without colliding is

$$df(l) = -Ke^{-Kl} dl. \quad (22)$$

The path available is thus solely a function of  $f(l)$ , so that the average path is

$$\lambda = \frac{\int_Q^\infty l df(l)}{\int_Q^\infty df(l)}. \quad (23)$$

On integration, we thus have

$$\lambda = (1/K) + Q \quad (24)$$

and therefore  $f(l) = e^{-l(\lambda-Q)} + 1 - e^{-Q(\lambda-Q)}$ . (25)

These expressions naturally reduce to the classical formulae when  $Q$  is taken to be zero. Denoting by  $\lambda_\infty$  the value of  $\lambda$  which would be obtained without the imposition of a lower limit to the free path, we see that  $K = 1/\lambda_\infty$ , and that

$$\lambda = \lambda_\infty + Q. \quad (26)$$

The effect of the imposition is thus to yield an expression for the mean free path which is greater than the classical value by the distance,  $Q$ ; hence

$$\lambda = \lambda_\infty \left( 1 + \frac{Q}{\lambda_\infty} \right). \quad (26)$$

We next inquire into the general expression for the average velocity, which, according to classical theory, is related as follows to the average kinetic energy

$$v = 4 \left( \frac{\epsilon_{\text{kin}}}{3\pi m} \right)^{\frac{1}{2}}. \quad \text{I (15)}$$

† See Born, *Atomic Physics*, p. 339, Blackie, (1935).

Now the average energy of a three-dimensional oscillator with a vibration frequency  $\nu$  is

$$\epsilon = \frac{3h\nu}{2} \coth \frac{h\nu}{2kT}, \quad (27)$$

and the average kinetic energy of such an oscillator is one-half of this value, so that

$$v = 2\left(\frac{h\nu}{\pi m} \coth \frac{h\nu}{2kT}\right)^{\frac{1}{2}}. \quad (28)$$

We thus have, using the Boltzmann-Tait expression for  $\lambda_\infty$ , the general collision equation

$$Z = \frac{2\pi\sigma^2 n \left( \frac{2h\nu}{\pi m} \coth \frac{h\nu}{2kT} \right)^{\frac{1}{2}}}{1 + \sigma^2 n (2h/\pi m\nu)^{\frac{1}{2}}}. \quad (29)$$

When the molecular concentration,  $n$ , is large, this reduces to

$$Z = 2\pi\nu \left( \coth \frac{h\nu}{2kT} \right)^{\frac{1}{2}}, \quad (30)$$

which is clearly independent of the concentration. At the absolute zero of temperature,  $Z = 2\pi\nu$ . In a condensed system of weak oscillators, we also have, by expansion, the approximate relation

$$\begin{aligned} Z &= 2\pi(2\nu k T / h)^{\frac{1}{2}} \\ &= 4\pi \left( \frac{kT}{h} \frac{\epsilon_0}{3h} \right)^{\frac{1}{2}}. \end{aligned} \quad (31)$$

When, on the other hand, the molecular concentration is low and the temperature high, equation (29) clearly reduces to

$$Z = 4\pi\sigma^2 n \sqrt{\frac{kT}{\pi m}}, \quad I(19)$$

which is the gas collision formula. To within the same degree of approximation the viscosity is seen to be linearly related to the density:

$$\eta = \frac{2}{3\pi\sigma^2} \left( \frac{mkT}{\pi} \right)^{\frac{1}{2}} \left[ 1 + \sigma^2 n \left( \frac{2h}{\pi m\nu} \right)^{\frac{1}{2}} \right]. \quad (32)$$

### *The Frequency of Ionic Collisions in Solution*

None of the collision formulae discussed so far is applicable, without further justification, to the determination of the frequency of collisions between ions in solution. In Chapter IV, it is true, we assumed that the gas collision formula was valid, but the theory could have been equally well developed with the aid of any other collision

equation, because the influence of electrostatic forces was there attributed, not to a hastening of the mutual approach of any two oppositely charged ions but to a modification of the concentration of ions of one sign in the neighbourhood of ions of another sign.<sup>†</sup>

Langevin's method for determining the frequency of ionic collisions in gases,<sup>‡</sup> which has been applied to the problem in hand,<sup>§</sup> has the merit of not requiring a knowledge of the ionic radii. The number of ions of type *B* which, in unit time, cross the spherical boundary of extension  $4\pi R^2$  surrounding a given ion *A* is clearly  $4\pi R^2 n_B v$ , where *v* is the relative velocity of approach (see the derivation of equation I(19)). The total number of approaches to within this distance is  $\frac{1}{2}n_A$  as great, so that

$${}_A Z_B = 2\pi R^2 n_A n_B v. \quad (33)$$

Taking, for example, two univalent ions of opposite charges, the force exerted between them is  $-\epsilon^2/DR^2$ . The velocity of ion *A* is thus  $v_A = -(\epsilon^2/DR^2)/S_A$ , where  $S_A$  is a resistance factor given, for spherical molecules, by Stokes's law. The velocity of ion *B* is similarly  $(\epsilon^2/DR^2)/S_B$  in magnitude, but opposite in sign, so that the relative velocity is

$$v = \frac{\epsilon^2}{DR^2} \left( \frac{1}{S_A} + \frac{1}{S_B} \right)$$

$$= v_A + v_B,$$

and, consequently,

$${}_A Z_B = 2\pi R^2 n_A n_B (v_A + v_B). \quad (34)$$

Now the ionic mobility, *u*, is defined as the velocity of migration of an ion in a field, *F*, of unit strength:<sup>||</sup>

$$u = v/F, \quad (35)$$

and is known from Kohlrausch's law and the molar conductances. Moreover, since *F* in the present case is assumed to be  $\epsilon/DR^2$ , we have  $v = Fu = (\epsilon/DR^2)u$ , so that

$${}_A Z_B = 2\pi n_A n_B \epsilon (u_A + u_B)/D. \quad (36)$$

Except for the dielectric constant, *D*, and an unimportant numerical

<sup>†</sup> Christiansen, *Z. physikal. Chem.*, **113**, 35, (1925); Scatchard, *Chem. Rev.*, **10**, 229, (1932); Moelwyn-Hughes, *Proc. Roy. Soc., A*, **155**, 308, (1936).

<sup>‡</sup> *Ann. Chim. Physique*, **28**, 28, (1903).

<sup>§</sup> Moelwyn-Hughes, *Trans. Faraday Soc.*, **34**, 91, (1938).

<sup>||</sup> In practical units, *u* is the velocity in a field of one volt-electron per cm., i.e. under the influence of a force of  $1.59 \times 10^{-12}$  dyne.

factor, this is Langevin's equation. On applying it to collisions between elementary univalent ions in aqueous solution, we find values somewhat smaller than those given by the simple collision equation. For collisions between potassium and chloride ions, for example,  $AZ_B$  at 20° C. becomes  $6.5 \times 10^9$  litres/gram-ion-second, and even in the case of the mobile ions,  $H^+$  and  $OH^-$ , the figure is not more than  $2.5 \times 10^{10}$ .

Rather than merely guess that the collision frequency between ions which react chemically is higher than that given by Langevin's equation for ions that do not react, we may estimate the former quantity from experimental data as follows. We have shown that for ionic reactions,

$$AZ_B = Ae^{+z_A z_B e^2/LDr}, \quad \text{III (4) and IV (6)}$$

where  $Z$  is some constant having the dimensions of a binary collision frequency,  $A$  is first of the two empirical constants of the Arrhenius equation,  $D$  is the dielectric constant,  $r$  the critical distance of ionic approach, and  $L$  is the reciprocal of Abegg's temperature (Table IV (1)). Let us then choose a pair of ionic reactions, such as the ammonium-cyanate and the bromide-thiosulphate reactions, for which we know that  $r$  cannot be very different. The products  $z_A z_B$  and  $z_P z_Q$  of the ionic charges are, however, different and so, for that reason, are the constants  $A_{A,B}$  and  $A_{P,Q}$ . In the present pair of reactions, they are, respectively,  $-1$ ,  $+2$ ,  $1.92 \times 10^{+8}$ , and  $3.49 \times 10^{+12}$ . On solving for  $Z$  we find

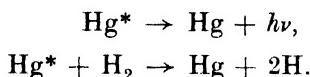
$$\ln Z = \left( \frac{z_P z_Q}{z_P z_Q - z_A z_B} \right) \ln A_{A,B} - \left( \frac{z_A z_B}{z_P z_Q - z_A z_B} \right) \ln A_{P,Q}, \quad (37)$$

which gives a numerical value of  $6.20 \times 10^{11}$  litres/gram-ion-seconds. The original assumption that the gas collision formula is valid cannot, therefore, be very far removed from the truth.

### *The Frequency of Inelastic Collisions in Solution*

The collisions with which we have been chiefly concerned up to the present are the so-called activating ones, in which the kinetic energies, and sometimes the oscillatory energies of the partners are momentarily converted into potential energy. The conditions governing the transfer of energies during molecular collisions are as yet but dimly understood. The calculation of the probability of the transference of a given amount of energy from one oscillator to another, and the problem of the excitation of vibrational quanta have been developed

from different angles.<sup>†</sup> From the experimental point of view our knowledge is less meagre concerning the still more intricate problem of the conversion, during collision, of electronic energy into other kinds of energy. The theory of the vibrational excitation of normal molecules by collision with electronically excited atoms<sup>‡</sup> has been amply verified<sup>§</sup> for gaseous reactions. An excited mercury atom, for example, can lose its energy not only by the emission of a quantum,  $h\nu$ , of radiation, but by a radiationless transfer of energy to a hydrogen molecule, which it thereby dissociates:



The chance of the latter process occurring obviously increases with an increase in the concentration of hydrogen. Experiments with other diatomic molecules show also that the most efficient robbers of the electronic energy are those molecules which require for their dissociation an energy lying near to the energy of the quantum,  $h\nu$ , which the atom can emit without impact.

The entirely analogous phenomena of fluorescence and photo-sensitization have been extensively studied in solution.

### 1. *The Quenching of Fluorescence*

A system is said to fluoresce when, simultaneous with the absorption of radiation of a given wavelength, it emits radiation of longer wavelength. Chlorophyll in water is the best-known example. Although many hypotheses, including that of ionization,<sup>||</sup> have been advanced to explain fluorescence in solution, the generally accepted theory<sup>††</sup> is based on the idea of radiationless transfers between molecules of the fluorescent solute and other molecular species in solution.

Let us, using the stationary state hypothesis (p. 17), consider the formation of electronically excited molecules,  $A^*$ , by the absorption of radiation at a rate,  $k_3 n_A$ , which is taken to be proportional to the concentration,  $n_A$ , of ordinary, unexcited molecules,  $A$ . The value of  $k_3$  is determined by the nature and intensity of the exciting radiation

<sup>†</sup> Zener, *Phys. Rev.*, **38**, 277, (1931); Mott and Massey, *The Theory of Atomic Collisions*, Oxford University Press, (1932); Eucken and Beck, *Z. physikal. Chem.*, **B**, **29**, 219, (1934).

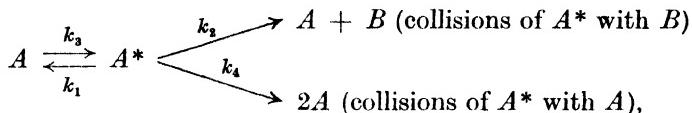
<sup>‡</sup> Klein and Rosseland, *Z. Physik*, **4**, 46, (1921).

<sup>§</sup> Cario and Franck, *ibid.*, **21**, 162, (1922).

<sup>||</sup> B. E. Buckingham, *Z. physikal. Chem.*, **19**, 129, (1894).

<sup>††</sup> Wawilow, *Z. Physik*, **31**, 750, (1925).

and by the dimensions and design of the reaction vessel. The excited molecules may lose their energy by the spontaneous emission of the fluorescent light at a rate  $k_1 a$ , where  $a$  is their concentration, and  $k_1$  their decay constant, or the reciprocal of their mean life. They may also, it is postulated, lose energy by radiationless transfer during binary collisions with normal molecules of their own kind, and with other molecules in the solution. According to the scheme



the rate of formation and destruction of excited molecules is

$$+\frac{da}{dt} = k_3 n_A - k_1 a - k_2 n_B a - k_4 n_A a,$$

which is zero when a stationary state has been reached. We thus have

$$a = \frac{k_3 n_A}{k_1 + k_2 n_B + k_4 n_A}.$$

The rate of emission of light is therefore

$$I = k_1 a = \frac{k_1 k_3 n_A}{k_1 + k_2 n_B + k_4 n_A}. \quad (38)$$

In the absence of any added quenching solutes this rate has its maximum value of

$$I_0 = \frac{k_1 k_3 n_A}{k_1 + k_4 n_A}.$$

Consequently,  $\frac{I}{I_0} = \frac{k_1 + k_4 n_A}{k_1 + k_2 n_B + k_4 n_A} \quad (39)$

and the quenching coefficient is

$$Q = 1 - \frac{I}{I_0} = \frac{k_2 n_B}{k_1 + k_4 n_A + k_2 n_B}. \quad (40)$$

Except for the term  $k_4 n_A$ , which we have included to account for self-quenching, this is the equation derived by Stern and Volmer† in their study of sensitized fluorescence in the gaseous phase, and by Wawilow‡ in his study of the same phenomenon in solution.

Some of the values obtained, by a variety of methods into the details of which we cannot here enter, for the average lifetime

† *Physikal. Z.*, **20**, 183, (1919).

‡ *Z. Physik*, **31**, 750, (1925).

of the excited molecules of some familiar fluorescent substances in aqueous solution are given in Table 3.

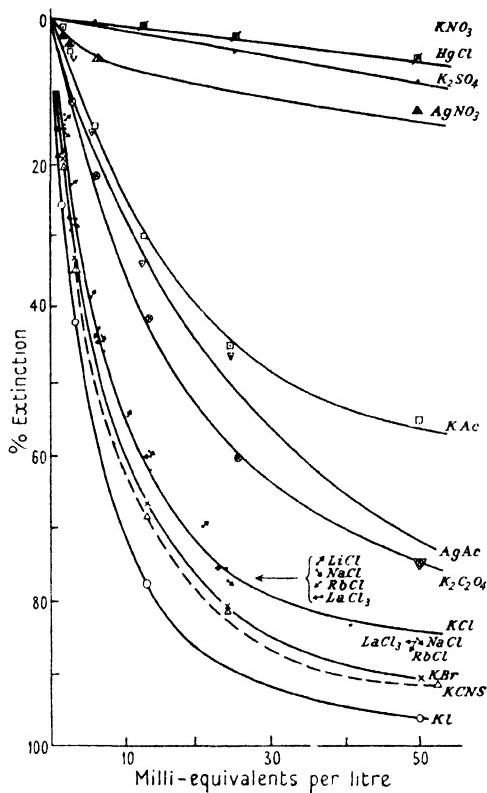


FIG. 1.

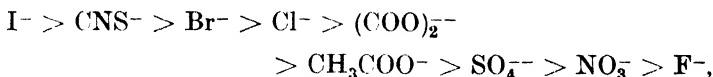
Table 3

Fluorescent substance	Average lifetime, $\tau$ (seconds)	Authority
Fluorescein	$4.5 \times 10^{-9}$	Perrin, <i>Journal de Physique</i> , 7, 390, (1926)
Uranine (di-sodium salt)	$5.0 \times 10^{-9}$	Gaviola, <i>Z. Physik</i> , 42, 862, (1927)
Quinine bisulphate	$(9.5 \pm 2.0) \times 10^{-8}$	Wawilow, <i>ibid.</i> , 53, 665, (1929)

The specificity of the quenching process is well illustrated in Fig. 1, which is taken from the work of Jette and West.<sup>†</sup> This systematic investigation, making use of compensating photoelectric cells to

<sup>†</sup> *Proc. Roy. Soc., A*, 121, 299, (1928).

measure the intensity of fluorescence, has established a number of interesting points. Quite clearly, the quenching is due to the anions, with the possible exception of the silver cation: thus chlorides of various metals have the same effect in solutions of equivalent strength; and mercuric chloride, which is largely un-ionized, has little effect. The most efficient quencher of fluorescence is the iodide ion. In the order of diminishing effectiveness in quenching the radiation, the ions arrange themselves as follows:



which is also the order of diminishing polarizability† and coagulation power.‡ The ability of an ion to deactivate an electronically excited molecule is thus closely connected with the looseness of attachment of the electrons in the ion.

On inverting equation (39) we see that the ratio of the intensity of fluorescence in the absence of a quenching material to that in the presence of a quencher,  $B$ , is linearly related to the concentration of the latter:

$$\frac{I_0}{I} = 1 + \left( \frac{k_2}{k_1 + k_4 n_B} \right) n_B. \quad (39)$$

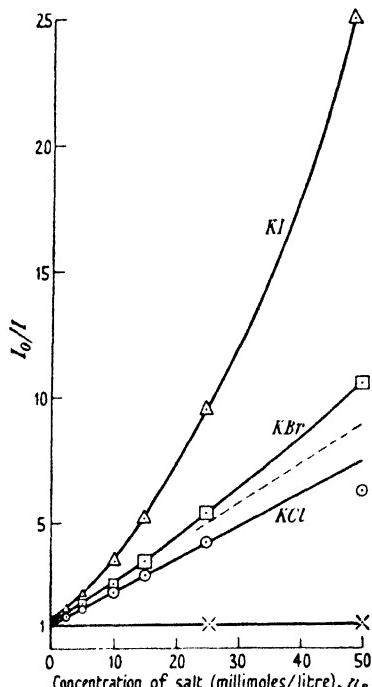
This method of analysis, proposed by Wawilow, has been applied in Fig. 2 to the data of Jette and West on the quenching of the fluorescence of quinine hydrogen sulphate in the presence of varying amounts of potassium halides in aqueous solution at room temperatures. There

FIG. 2. The quenching of the fluorescence of quinine by halide ions in water.

is a strong tendency to linearity in the region of low concentration. Omitting the self-quenching factor, the initial gradients yield values

† Fajans and Joos, *Z. Physik*, **23**, 1, (1924).

‡ Heydweiler, *Ann. Physik*, **41**, 499, (1913).



for the ratio  $k_2/k_1$ . Results obtained in this way (Table 4) are more reliable than those given by the alternative method of interpolating the concentration,  $n'_B$ , required to reduce the fluorescent radiation to

Table 4

*An Application of Wawilow's Theory to the Quenching of the Fluorescence of the Quinine Ion in Water*

Electrolyte	$(k_2/k_1)$ (litres/gm. mole)	$k_1$ (litres/gm. mole.sec.)	$r_A/r_B$
KCl	150	$1.58 \times 10^9$	1.92
KBr	178	$1.87 \times 10^9$	2.27
KI	200	$2.10 \times 10^9$	2.55

50 per cent. of its uninhibited value. This concentration, from equation (40), is seen to be

$$n'_B = \frac{k_1}{k_2} + \frac{k_4}{k_2} n_A. \quad (41)$$

By combining with the decay constant ( $k_1 = 1/\tau$ ) given in Table 3, we evaluate the essentially bimolecular velocity coefficients,  $k_2$ . Their magnitude is recognized at once to be considerably less than the collision frequency afforded by the gas formula. We may therefore conclude either that the deactivation process is a relatively inefficient one, or that the frequency of collision is slow and due to the process of diffusion. If the latter supposition is correct, we may compare the values of  $k_2$  with that resulting from equation (4), which, in litres per gram molecule per second, is

$$k_2 = \frac{kT}{3\eta} \frac{(r_A+r_B)^2}{r_A r_B} \frac{N_0}{1000}. \quad (42)$$

As the fluorescing molecule is generally larger than the ion with which it collides, we may approximate further to

$$k_2 = \frac{kT}{3\eta} \frac{r_A}{r_B} \frac{N_0}{1000}. \quad (43)$$

Assuming the experiments of Jette and West to refer to pure water at 20° C., for which  $RT/3000\eta$  is  $8.23 \times 10^8$ , we obtain the ratios of the radii of the quencher and the deactivating ion shown in Table 4. If we take  $r_A$  to be, on an average, equal to  $2r_B$ , the calculated value of  $k_2$  becomes  $3.70 \times 10^9$ , and the deactivating efficiencies vary from about 0.5 ( $\text{Cl}^-$ ) to 0.6 ( $\text{I}^-$ ).

As further evidence for his theory, Wawilow† has measured  $I_0/I$

† *Z. Physik*, 53, 665, (1929).

for the quinine sulphate system in water containing fixed concentrations of quinine and potassium iodide at temperatures ranging from 16° to 95° C., and has established experimentally the proportionality between  $I_0/I$  and  $T/\eta$  required by equation (42).† Halide ions thus appear to be efficient deactivators, compared with the nitrate ion, for which  $P$  is about  $10^{-3}$ . A complete set of such calculations has been made by Doss,‡ who has also discussed the question of specificity in deactivation.

We have used the word 'molecule' to describe the fluorescent substance, though in fact it must, from the nature of the salts used, be an ion. The influence of added electrolytes and of media of varying dielectric capacity on the quenching of fluorescein does, in fact, indicate that the former effects can be accounted for quantitatively by the Bjerrum-Brönsted theory and the latter qualitatively by Scatchard's theory (equations (12) and (25) of Chapter IV).§ Silver ion apparently acts in the anticipated direction. If, however, the deactivation mechanism under discussion has all the normal features of a bimolecular reaction between ions, we are provided with an alternative explanation of the frequency and apparent inefficiency of collisions by the complete theory developed in Chapter IV. We can now, for example, regard the experimental value of  $k_2$  as being lower than the collision frequency by a factor of about  $10^2$ , according to equation IV(6), and the proportionality between the ratio ( $k_1/k_2$ ) and the viscosity as indicating a direct dependence of  $k_1$  upon this variable. Although it is difficult to disentangle all the effects involved, there appears an undisputed parallelism between deactivating collisions in the gaseous phase and in solution,|| and evidence that in both phases the rate at which the energetically well-endowed solutes are impoverished by collisions is determined by the process of diffusion.

## 2. Photochemical Reactions

Some slight evidence, bearing more obliquely on our problem, is afforded by a comparison of direct photolyses and photosensitized reactions in the gaseous phase and in solution.

† In the present account of Wawilow's work, I have changed the notation, and the units from those of grams/c.c. used by him.

‡ *Proc. Indian Acad. Sci.*, **6**, 24, (1937).

§ Stoughton and Rollefson, *J. Amer. Chem. Soc.*, **62**, 2264, (1940).

|| See also Frank and Levi, *Z. physikal. Chem.*, **B**, **27**, 409, (1934); Schneider, *ibid.*, **B**, **28**, 311, (1935).

The general theory of activation merely demands that only molecules in an exceptional state shall undergo chemical change, and does not specify the manner in which ordinary molecules can enter that state. In thermal reactions, as we have seen, molecules become activated by the redistribution of energy during impacts. In photochemical reactions, radiation absorbed by the molecules from an external source supplies the necessary energy. The Stark-Einstein law of photochemical equivalence states that, in a photosensitive system illuminated by radiation of frequency  $\nu$ , one molecule decomposes for each quantum  $h\nu$  of energy absorbed. In this simple form the law is true in a few cases only, but there is evidence that it is applicable to the primary process in all photochemical reactions.<sup>†</sup> Generally, therefore, the rate of the primary process, and in certain cases the rate of chemical change also, is simply the rate at which the molecules absorb radiation, but the total course of photochemical change may have varying degrees of complexity, depending on the relative influence of the subsequent 'dark' reactions.

The kinetics of reaction, as the term is understood in connexion with thermal processes, do not therefore occupy as prominent a place in the study of photochemical reactions as the determination of the quantum efficiency. This is defined as the ratio of the number of molecules decomposed to the number of light quanta absorbed, or

$$\gamma = \frac{\text{number of molecules decomposed}}{\text{number of molecules activated in the primary process}}.$$

In the majority of cases which have been examined, the activated molecule produced by the absorption of radiation, or an atom resulting from the dissociation of this activated molecule, is able to bring about the decomposition of a second molecule of reactant. Frequently also the primary process is but the initiation of a reaction chain wherein several molecules are transformed. For our purpose, however, we are less concerned with the actual quantum yield than with the manner in which it may be influenced by the presence of a solvent.

For each quantum of radiation absorbed by gaseous hydrogen iodide in the spectral region 2,070–2,820 Å., two molecules decompose, this number being independent of temperature.<sup>‡</sup> The following

<sup>†</sup> Griffith and McKeown, *Photoprocesses in Gaseous and Liquid Systems*, Longmans, London, (1929); Bonhoeffer and Harteck, *Photochemie*, Steinkopff, Leipzig, (1933).

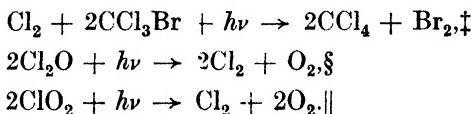
<sup>‡</sup> Bodenstein and Lieneweg, *Z. physikal. Chem.*, **119**, 123, (1926).

mechanism of the reaction, proposed by Warburg,<sup>†</sup> is now regarded as established:

1.  $\text{HI} + h\nu \rightarrow \text{H} + \text{I}$
2.  $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$
3.  $\text{I} + \text{I} \rightarrow \text{I}_2$ .

In the liquid state also the quantum efficiency is 2.

The following direct photolyses, involving absorption of light of wavelength 4,100 to 4,500 Å. (i.e. about 66,000 calories per gram molecule), have all a quantum efficiency of 2, both in the gaseous phase and at all measurable dilutions in carbon tetrachloride solution:



A quantum efficiency of nearly one has been found for the decomposition of oxalyl bromide in the same two phases.<sup>††</sup> Values of  $\gamma$  which are independent of the dilution have also been found for the bromine-sensitized oxidation of monobromtrichlormethane,<sup>†††</sup> the chlorination of the same compound,<sup>§§</sup> and for the bromine-sensitized conversion of diethyl maleate into diethyl fumarate,<sup>|||</sup> for which  $\gamma = 295$ .

For the photolysis of hydrogen iodide in hexane solution,  $\gamma$  was found to have a value of 2 only at concentrations exceeding one mole or so per litre. A similar behaviour is exhibited by the photolytic reaction between diazoacetic ester and iodine<sup>††††</sup> in carbon tetrachloride solution (Fig. 3), and is of fairly common occurrence. The explanation, according to Warburg and Rump,<sup>††††</sup> is to be sought in the diminished probability of the secondary collisions taking place at high dilutions.

From the two sets of phenomena, it is to be concluded that free atoms and excited molecules can be generated photolytically with the same ease in the dissolved state as in the gaseous state, though

<sup>†</sup> *Sitzungsber. Preuss. Akad.*, 314, (1916).

<sup>‡</sup> Noddack, *Z. Elektrochem.*, 27, 359, (1921); Grüss, *ibid.*, 29, 144, (1923).

<sup>§</sup> Bowen, *Trans. Chem. Soc.*, 123, 2330, (1923); Bodenstein and Kistiakowsky, *Z. physikal. Chem.*, 116, 371, (1925); Schumacher and Wagner, *ibid.*, B, 5, 199, (1929); Dickenson and Jeffreys, *J. Amer. Chem. Soc.*, 42, 4288, (1930).

<sup>||</sup> Booth and Bowen, *Trans. Chem. Soc.*, 127, 510, (1925); Bodenstein, Harteck, and Padelt, *Z. anorg. Chem.*, 147, 233, (1925).

<sup>††</sup> Atwood and Rollefson, *J. Chem. Physics*, 9, 506 (1941).

<sup>†††</sup> Grüss, *loc. cit.*

<sup>§§</sup> Noddack, *loc. cit.*

<sup>††††</sup> Eggert and Borinski, *Physikal. Z.*, 24, 504, (1923); 25, 19, (1924).

<sup>††††</sup> Newling, Staveley, and Moelwyn-Hughes, *Trans. Faraday Soc.*, 29, 1155, (1933). <sup>††††</sup> *Z. Physik*, 47, 305, (1928).

complicating side reactions are naturally more likely to intrude in solution.

The uranyl ion has long been known to render the decomposition of oxalic acid sensitive to light of the visible and ultra-violet regions

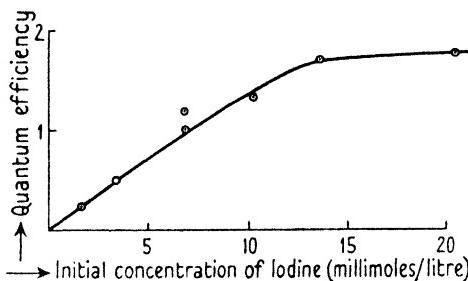


FIG. 3.

of the spectrum. Ions which are efficient deactivators of the electronically excited uranyl ion have been found to be efficient also as inhibitors of the decomposition of oxalates,<sup>†</sup> and fall into the same (lyotropic) series. These and similar experiments on photosensitization prove that electronic energy can be utilized in effecting chemical changes in solution, but the problem of the nature of these special kinds of collisions cannot here be discussed.<sup>‡</sup>

A solute molecule may be photochemically decomposed without the acquisition of much kinetic energy. The fragments formed may thus collide with each other within the solvent sheath before separating. The occurrence of such a specialized type of repetitive collision<sup>§</sup> can in large measure account for the difference in quantum yields of ketone decompositions in the gas phase and in solution.<sup>||</sup> It is doubtful, however, how far the idea of repetitive collisions can be extended to thermal reactions or to other collision phenomena in solution. On the whole, the evidence is against such an extension.<sup>††</sup>

### Discussion

It would be folly to pretend that any single theory can be found to embrace all the different kinds of molecular collisions known in solution.

<sup>†</sup> West, Müller, and Jette, *Proc. Roy. Soc., A*, **121**, 294, (1928).

<sup>‡</sup> See Bonhoeffer and Harteck, *Grundlagen der Photochemie*, Steinkopff, (1933).

<sup>§</sup> Franck and Rabinowitch, *Trans. Faraday Soc.*, **30**, 120, (1934); Rabinowitch and W. C. Wood, *ibid.*, **32**, 1381, (1936).

<sup>||</sup> Bamford and Norrish, *Trans. Chem. Soc.*, 1531, (1938).

<sup>††</sup> Farkas and Garbatski, *ibid.*, **35**, 263, (1939).

Two distinct groups of experiments prove that the frequency of binary collisions between solute molecules undergoing chemical change has the same order of magnitude as, and in fact lies very close to, the frequency as calculated by the simple kinetic theory. They are, it will be recalled, the direct comparison of rates of bimolecular chemical reactions in the gaseous phase and in solution, and the absolute magnitude of the velocity of ionic reactions. Two other distinct groups of experiments prove that the frequency of binary collisions between ions which do not react chemically and between electronically excited and deactivating solutes is lower by a factor of approximately 100. This conclusion is based on the electrical conductances of ions and upon the efficiency of the quenching of fluorescent radiation. There is no incompatibility between the two conclusions, and it seems necessary to emphasize that one set of phenomena may well be interpreted in terms of a given theory without detriment to the validity of a completely different interpretation in other cases.

The key to the situation is provided by the knowledge of how much kinetic energy is, on the average, available for the colliding molecules. In the quenching phenomena, the migration of ions without chemical change, the coagulation of hydrosols, and probably in the termination of reaction chains,† no exceptional energy is necessary to effect the changes involved. Such kinetic energy as is available is utilized in the struggle of the solute molecule to get outside its sheath of solvent neighbours, and so to diffuse slowly to the neighbourhood of its partner. Quite a different state of affairs prevails when chemical reaction takes place, for in activating collisions the molecules possess considerable kinetic energy. The amount of this energy, given, with modifications, by the Arrhenius constant  $E_A$ , generally greatly exceeds the heat of vaporization of the solute. The activated solute molecule thus moves about in the liquid at least as freely as it would in the gaseous phase. The barrier which must be surmounted before it can leave one solvent envelope for another represents only a fraction of the total energy of activation. Molecules which are to react chemically do not generally walk towards one another, as in diffusion and other physical changes, but rush at one another.

† E.g., the catalysed polymerization of methyl methacrylate; Norrish and R. R. Smith, *Nature*, **150**, 336, (1942).

As stated, no single formula must be expected to cope with the diversity of effects under consideration, but, for the sake of summarizing the position with slightly greater precision, we may look at it in the light of the axiomatic relationship

$$_A Z_B = 2\pi R^2 n_A n_B v, \quad (33)$$

where  $R$  is the distance apart of the centres of the colliding molecules,  $n_A$  and  $n_B$  are their concentrations, and  $v$  is their average relative velocity. For ions approaching one another under the influence of Coulombic attraction, we have, in terms of the electronic charge,  $\epsilon$ , the equivalent conductivity,  $\Lambda_\infty$ , at infinite dilution, the dielectric constant,  $D$ , and Faraday's constant,  $F$ ,

$$v = \frac{\epsilon \Lambda_\infty}{DR^2 F}. \quad (44)$$

For molecules suffering thermal diffusion, we have

$$v = (D_A + D_B)/R = kT/6\pi\eta r_A r_B, \quad (45), (3)$$

where  $D_A$  and  $D_B$  are the coefficients of diffusion. Finally, for molecules possessing only kinetic energy, the average relative velocity is

$$v = 2\left(\frac{kT}{2\pi\mu}\right)^{\frac{1}{2}}, \quad (46)$$

where  $\mu$  is the reduced mass. By substituting these expressions in equation (33), we recover the formulae of Langevin,

$$_A Z_B = 2\pi n_A n_B \epsilon \Lambda_\infty / DF; \quad (36)$$

of Smoluchowski,

$$_A Z_B = 2\pi R n_A n_B (D_A + D_B); \quad (2)$$

of Wawilow,  $_A Z_B = (kT/3\eta) n_A n_B (r_A + r_B)^2 / r_A r_B;$  (4)

and of the kinetic theory of gases,

$$_A Z_B = R^2 n_A n_B \left(\frac{8\pi kT}{\mu}\right)^{\frac{1}{2}}. \quad \text{I} (21)$$

When the difference between the total energy,  $E$ , and the potential energy,  $U$ , greatly exceeds the equipartition value, we obtain the formula

$$_A Z_B = \pi R^2 n_A n_B [8(E - U)/\mu]^{\frac{1}{2}}, \quad (47)$$

which illustrates how attraction enhances and how repulsion diminishes the frequency of collisions.

## IX

### UNIMOLECULAR REACTIONS

IN one sense, unimolecular reactions in solution are easier to understand than bimolecular reactions in solution or unimolecular reactions in gases. The first necessity for chemical change is the accumulation of a critical energy, and most solvent molecules are able to assist in this direction whenever a solute molecule is structurally capable of undergoing intramolecular change. The role of the solvent, however, need not be exclusively that of an activator: it can, in addition, modify the energy of activation itself (p. 27), and exert other influences, an investigation of which forms the subject of this chapter.

The stationary state hypothesis, amplified by the inclusion of terms to account for the influence of the solvent, leads to a general equation for the kinetics of uncomplicated reactions of the first and second order in solution. Let

$c$  = concentration of solute,

$s$  = concentration of solvent, and

$a$  = concentration of activated molecules of solute.

Then

$$\text{rate of activation} = k_1 cs + k_2 c^2,$$

$$\text{rate of deactivation} = k_3 as + k_4 ac, \text{ and}$$

$$\text{rate of chemical reaction} = k_5 a.$$

The condition for a stationary concentration of active molecules is  $k_1 cs + k_2 c^2 = k_3 as + k_4 ac + k_5 a$ . The velocity of chemical change is thus

$$-\frac{dc}{dt} = k_5 a = \frac{k_5(k_1 cs + k_2 c^2)}{k_3 s + k_4 c + k_5}. \quad (1)$$

Of the five constants concerned, three are primarily characteristic of the reaction itself and two ( $k_1$  and  $k_3$ ) are functions of the solvent also. The relative magnitudes of these constants determine the order of reaction and the extent of the solvent effect.

In a completely inert solvent, active molecules of solute are neither formed nor destroyed by collisions with solvent molecules (i.e.  $k_1 = 0$  and  $k_3 = 0$ ). Under these conditions, the velocity ( $v$ ) of reaction, is

$$v = \frac{k_5 k_2 c^2}{k_4 c + k_5}. \quad (2)$$

Two special cases must be discussed. When the chance of an active solute molecule losing its energy by collision with a normal solute molecule is small, the expression reduces to  $k_2 c^2$ , and the rate is a simple bimolecular one. The decomposition of chlorine monoxide in carbon tetrachloride solution furnishes an example. When collisions between active and normal solute molecules are highly efficient in the deactivating sense ( $k_4 \gg k_5$ ), the expression becomes  $(k_5 k_2/k_4)c$ , and the rate is a simple unimolecular one. The decomposition of nitrogen pentoxide and the isomerization of pinene in carbon tetrachloride solution conform to these conditions. The experimental observation that the velocities of these reactions are the same in the gaseous phase as in solution in this solvent shows that not only has  $k_5$  remained unchanged, as might be expected, but that the ratio of the constants  $k_2$  and  $k_4$  also is unaffected by the solvent. Both these depend upon collision frequencies, which must therefore be similarly affected in the gas phase as in solution.

Positive and negative catalytic solvents are those in which active molecules of solute are generated or destroyed by collisions with molecules of the solvent. When solute-solvent collisions predominate over solute-solute collisions (i.e.  $k_2 \doteq 0$  and  $k_4 \doteq 0$ ),

$$v = \frac{k_5 k_1 c s}{k_3 s + k_5}, \quad (3)$$

and the reaction is unimolecular. Two special cases again arise. In true unimolecular reactions, when the vast majority of active molecules lose their energy before being transformed ( $k_3 \gg k_5$ ), the rate becomes  $(k_5 k_1/k_3)c$ . The observed unimolecular constant is thus the product of the true reactivity ( $k_5$ ) and the ratio of two constants which denote the activating and deactivating efficiency of the solvent. Most complicated molecules undergoing unimolecular change in solution probably do so by this mechanism. The other case is that in which there are no deactivations ( $k_3 = 0$ ); the reaction is then essentially bimolecular, although unimolecular with respect to the solute:

$$v = k_1 c s. \quad (4)$$

Ozone in carbon tetrachloride, carbonyl sulphide in water, and numerous other fairly simple molecules are transformed in this way, each activating collision between a solute molecule and a solvent molecule leading to chemical change. The rate at which any given

reaction of this type proceeds, as well as the critical increment, naturally vary from solvent to solvent.

Based upon the simple assumption that all the molecular species in a liquid system collide with varying activating and deactivating efficiencies, equation (1) and the simpler equations derived from it are sufficiently elastic to cover a large number of the phenomena of solvent action. By ascribing a relatively long life to a pair of molecules in collision, the scheme can be extended to include complex formation.

#### *A Comparison of the Kinetics of Unimolecular Reactions in the Gas Phase and in Solution*

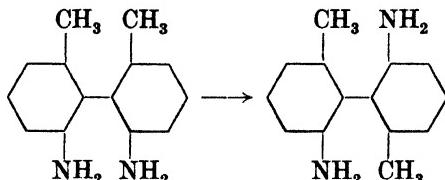
Very few of the many unimolecular reactions which have been investigated in the gaseous phase have been studied also in solution, probably because the temperature at which these changes take place with measurable velocity is usually higher than the boiling points of common solvents. As far as a comparison is possible, there is a striking similarity, in some cases amounting to identity, between the kinetics of unimolecular reactions in the two phases.

Unimolecular velocity constants for the gaseous decomposition of nitrogen pentoxide,



have been determined manometrically and colorimetrically in the gaseous phase and in a variety of solvents (Table 1). Only in two media does there appear a noticeable solvent effect, and this, it is thought, is due to the formation of a complex between solute and solvent.

The racemization of 2:2'-diamino-6:6'-dimethyldiphenyl



is a homogeneous unimolecular reaction in the gaseous phase and in diphenylether solution, with  $E_A$  values of 45,100 calories for the two systems.†

The anticipated change in kinetic order from the second to the

† Kistiakowsky and W. R. Smith. *J. Amer. Chem. Soc.*, **58**, 1042, (1936).

*Table 1*  
*The Decomposition of Nitrogen Pentoxide in Various Media*

Reference	Medium	$k_{10^\circ\text{C.}} \times 10^6$ (sec. <sup>-1</sup> )	$E_A$ (kilocal./mole)	$\ln_e A$
(1)	Gas	1.65	24.7	31.48
(2)	N <sub>2</sub> O <sub>4</sub>	3.44	25.0	32.82
(2)	CH <sub>3</sub> CHCl <sub>2</sub>	3.22	24.9	32.56
(2)	CHCl <sub>3</sub>	2.74	24.6	31.90
(3)	CHCl <sub>3</sub>	2.14	24.5	31.22
(2)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	2.38	24.4	31.42
(2)	CCl <sub>4</sub>	2.35	24.2	31.05
(3)	CCl <sub>4</sub>	2.34	24.5	33.09
(2)	CHCl <sub>2</sub> CCl <sub>3</sub>	2.20	25.0	32.35
(2)	Br <sub>2</sub>	2.15	24.0	30.61
(2)	CH <sub>3</sub> NO <sub>2</sub>	1.67	24.5	31.13
(2)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0.24	28.3	35.72
(2)	HNO <sub>3</sub>	0.05	28.3	34.11

- (1) Daniels and Johnston, *J. Amer. Chem. Soc.*, **43**, 53, (1921); White and Tolman, *ibid.*, **47**, 1240, (1925).  
 (2) Eyring and Daniels, *ibid.*, **52**, 1473, (1930).  
 (3) Lueck, *ibid.*, **44**, 757, (1922).

first, due to the constant high concentration of solvent, has been found in two cases. The decomposition of ozone



primarily a bimolecular reaction in the homogeneous gas phase, is unimolecular in carbon tetrachloride solution. The reaction between carbonyl sulphide and water,



predominantly bimolecular in the gaseous phase, is unimolecular in aqueous solution. Glycerol, urea, and other solutes which increase the viscosity, increase also the rate of hydrolysis in water. To compare the energies of activation (Table 2), the Guzman term *B* (p. 12) must be added to the apparent energy of activation found in the condensed phases.

One molecule of ozone out of every 17 that decomposes in solution reacts with the solvent, producing phosgene



and the hydrolysis of carbonyl sulphide is subject to some catalysis by ions in solution and by surfaces enclosing the gas. Other explanations for the difference in mechanism in the various media cannot, therefore, be excluded. We have merely given the most obvious one.

Where unimolecular reactions have been studied both in the

Table 2

*A Comparison of the Energies of Activation for Bimolecular Reactions in the Gaseous Phase which become Unimolecular Reactions in Solution*

Reference	Reaction	Phase	$E_A$ (kilocalcs./gm. mole)
(1)		Gas	27.8
(2)			30.9
(3)	$2\text{O}_3 \rightarrow 3\text{O}_2$	$\text{CCl}_4$	29.4 (mean)
(4)		Gas	26.2
(5)	$\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$	$\text{H}_2\text{O}$	28.6 (corrected)
			25.7
			23.3
			27.2 (corrected)

(1) Belton, Griffith, and McKeown, *Trans. Chem. Soc.*, **129**, 3153, (1926).

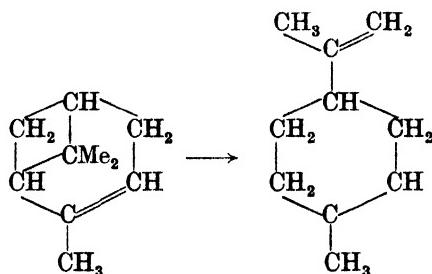
(2) Wulf and Tolman, *J. Amer. Chem. Soc.*, **49**, 1650, (1927).

(3) Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc., A*, **134**, 211, (1931).

(4) H. W. Thompson, Kearton, and Lamb, *Trans. Chem. Soc.*, 1033, (1935).

(5) Buchböck, *Z. physikal. Chem.*, **23**, 123, (1897).

gaseous and the pure liquid phases, there has also been found a marked indifference of the velocity of reaction to the physical state of the reactant. *d*-Pinene, for example, racemizes into *dl*-limonene† by a unimolecular mechanism



From polarimetric measurements in the homogeneous gas phase we have‡

$$\ln k = 33.77 - \frac{43710}{RT}.$$

The energy is probably reliable to within  $\pm 2,000$  calories. In the pure liquid phase at  $184.5^\circ\text{C}.$ , the reaction proceeds at a rate which is 36 per cent. faster; and in petrolatum solution over a range of temperatures,  $k$  is 48 per cent. greater than in the gas phase.  $E_A$  for the reaction in solution is 41,200 calories, by equation (1) of Chapter II. No real change has thus been detected between the Arrhenius

† Conant and Carlson, *J. Amer. Chem. Soc.*, **51**, 3464, (1929).

‡ D. F. Smith, *ibid.*, **49**, 43, (1927).

constants for the two systems. The same result is found in the unimolecular conversion of *iso*-stilbene ( $C_6H_5 \cdot CH=CH \cdot C_6H_5$ ) into the equilibrated mixture. In the gas we have†

$$\ln k = 29.4 - \frac{42800}{RT}.$$

That the reaction, though homogeneous, is not free from complications seems evident from the failure to reach the same equilibrium composition when starting from opposite directions. Experimental difficulties preclude the conversion in the liquid state from being examined over a region exceeding  $9^\circ$ . The velocity constant found‡ at  $214^\circ C.$  in the pure liquid is  $1.16 \times 10^{-6}$  sec. $^{-1}$ . That extrapolated from the Arrhenius equation for the gas reaction is  $0.38 \times 10^{-6}$ . Within the limits of error these rates are equal.

We conclude that solvents have, in general, but a slight influence on the velocity of unimolecular reactions, and that its magnitude is often no greater than can be accounted for by the variation, with respect to temperature and solvent, of the collision frequency between solute and solvent molecules. A simple mode of treatment thus seems possible.

#### *The Molecular Statistics of Uncomplicated Unimolecular Reactions in Solution*

The total number of collisions occurring per c.c. per second between molecules of solute of radius  $r$ , of mass  $m$ , and of concentration  $n$ , and molecules of a solvent with viscosity  $\eta$  is

$$Z = n \frac{3\pi r \eta}{m}. \quad I(28)$$

If each collision with energy equal to  $E$  results in chemical transformation, the rate of reaction becomes

$$-\frac{dn}{dt} = n \frac{3\pi r \eta}{m} e^{-E/RT},$$

giving a unimolecular constant

$$k = \frac{3\pi r \eta}{m} e^{-E/RT}. \quad (5)$$

The conditions envisaged are those corresponding to equation (4), i.e. there are no deactivations. The energy of activation is best found

† Kistiakowsky and Smith, *J. Amer. Chem. Soc.*, **56**, 638, (1934).

‡ T. W. J. Taylor and (Miss) A. R. Murray, *Trans. Chem. Soc.*, 2078, (1938).

by plotting  $\ln(k/\eta)$  against the reciprocal of the absolute temperature:

$$\ln(k/\eta) = \ln(3\pi r/m) - \frac{E}{RT}.$$

With unassociated solvents we may use equation I (31), and obtain directly

$$E = E_A + B. \quad (6)$$

This relationship, which ignores the slight change of density with temperature, has been applied to numerous reactions in solution,<sup>†</sup> of which a few are cited in Table 3. The values of the radii of the inorganic solutes have been obtained from extra-kinetic sources. The radius adopted for the monochloracetate ion is but a rough estimate; had we used the value (2.7 Å.) afforded by equation (17) of Chapter I, we would have obtained closer agreement. Without entering into too great detail, it is at once evident that collisions

Table 3

*The Molecular Statistics of some Simple Reactions in Aqueous Solution, involving Collisions between Solute and Solvent Molecules*

Reaction	$r \times 10^8$ (cm.)	$k_{25^\circ C.}$ (sec. <sup>-1</sup> )	$E$ (by eq. 5)	$E_A$ (calc.)	$E_A$ (obs.)
$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$	2.32	$2.75 \times 10^{-2}$	20,460	16,440	$16,800 \pm 400$ <sup>†</sup>
$\text{COS} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{H}_2\text{S}$	2.70	$2.05 \times 10^{-5}$	24,630	20,670	$23,260 \pm 1,600$ <sup>‡</sup>
$\text{O}_3 \rightarrow \frac{3}{2}\text{O}_2$ (in $\text{CCl}_4$ )	2.58	$3.93 \times 10^{-7}$	27,090	24,720	$26,160$ <sup>§</sup>
$\text{CH}_3\text{Cl}. \text{COO}^- + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}. \text{COO}^- + \text{Cl}^-$	3.0	$9.80 \times 10^{-10}$	30,330	26,950	$26,300$ <sup>  </sup>
					$27,100$ <sup>††</sup>

<sup>†</sup> Faurholt, *Z. anorg. Chem.*, **120**, 85, (1922); Brinkman, Margaria, and Roughton, *Phil. Trans.*, **A**, **232**, 65, (1933); Roughton and Booth, *Biochem. J.*, **32**, 2049, (1938); A. G. Mills and Urey, *J. Amer. Chem. Soc.*, **62**, 1019, (1940).

<sup>‡</sup> Buchböck, *loc. cit.*

<sup>§</sup> Proc. Roy. Soc., **A**, **134**, 211, (1931).

<sup>||</sup> Buchanan, *Berichte*, **4**, 340, (1871).

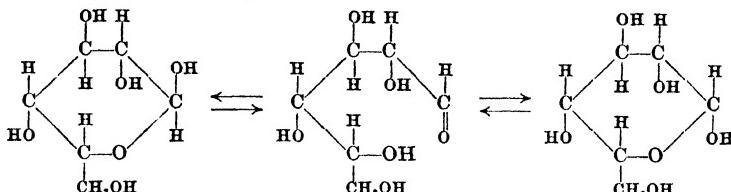
<sup>††</sup> Euler and Cassel, *Z. physikal. Chem.*, **84**, 371, (1913). See also Dawson and Dyson, *Trans. Chem. Soc.*, **49**, (1933); Reitz, *Z. physikal. Chem.*, **A**, **177**, 85, (1936).

between these solutes and the solvent molecules surrounding them are frequent enough to account for the rate of reaction. Moreover, the order of magnitude of the collision frequency is the same for many hydrolyses. The ratio of the absolute velocities of the fastest and slowest reactions ( $2.8 \times 10^7$ ) lies very near to  $e^{\Delta E/RT}$ , which, with  $\Delta E$  equal to 10,000 calories, is  $2.1 \times 10^7$  at  $25^\circ C$ .

<sup>†</sup> *Trans. Chem. Soc.*, **95**, (1932).

### The Mutarotation of Glucose in Water

The interconversion of  $\alpha$ -glucose and  $\beta$ -glucose is one of the simplest of chemical reactions, involving only the change in position of a hydrogen atom and a hydroxyl radical with respect to the plane of a pyranose ring:



The unimolecular constant,  $k$ , in pure water at 20° C., which is the sum of the constants,  $k_\alpha$  and  $k_\beta$ , for the two processes (p. 39), has long been regarded as a kinetic standard,<sup>†</sup> but doubt has remained for some time about the energy of activation. Early results<sup>‡</sup> indicated a value of 17,660 calories, for both the water reaction and the reaction as catalysed by hydrogen ion. A re-examination<sup>§</sup> confirmed the value of 17,600 for  $E_{H_2O}$  and gave  $E_{H_2O^+}$  as 19,300. Though neither of these values can be finally accepted, there is no doubt that the apparent energy of activation for the catalysed reaction exceeds that for the uncatalysed reaction, with which we are here concerned.  $E_{H_2O}$  varies with the temperature,<sup>||</sup> though not to so great an extent as results obtained in narrow temperature ranges suggest. The most extensive experiments<sup>††</sup> afford the values:

$$E_A(H_2O) = 16,945 \pm 18 \text{ calories, at } 298.1^\circ \text{ K.,}$$

$$k(H_2O) = (k_\alpha + k_\beta) = (2.473 \pm 0.006) \times 10^{-4} \text{ sec.}^{-1}, \text{ at } 293.1^\circ \text{ K.,}$$

and  $K = k_\alpha/k_\beta = 0.575 \pm 0.004.$

The last value, as far as kinetic measurements allow of a decision, is independent of temperature in the range 273° to 318° K.,<sup>††</sup> denoting a zero heat of reaction. Difficulties exist, of course, in determining the initial optical rotatory power of substances undergoing rapid changes, and the result may be slightly in error. In fact, the heat

<sup>†</sup> Riiber, *Berichte*, **56**, 2185, (1923); Richards, Lowry, and Faulkner, *Trans. Chem. Soc.*, 1733, (1927).

<sup>‡</sup> Hudson and Dale, *J. Amer. Chem. Soc.*, **39**, 320, (1917).

<sup>§</sup> Kilpatrick and Kilpatrick, *ibid.*, **53**, 3698, (1930).

<sup>||</sup> G. F. Smith and M. C. Smith, *Trans. Chem. Soc.*, 1413, (1937).

<sup>††</sup> Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc., A*, **176**, 352, (1940).

<sup>‡‡</sup> Nelson and Beagle, *J. Amer. Chem. Soc.*, **41**, 559, (1919).

of the acid-catalysed mutarotation, determined calorimetrically, appears to be  $\Delta H = -160$  calories.† It is not certain whether the same effect holds for the water reaction.‡ As its adoption leads to a standard entropy decrease ( $\Delta S^0 = -0.71$  cals./gm. mole-deg.) lying near to values found kinetically for xylose ( $-0.61$ ) and mannose ( $-0.84$ ), we may assume so provisionally, and proceed with the kinetic analysis as follows:

$$\left. \begin{aligned} k_\alpha &= k \frac{K}{K+1} = 0.903 \times 10^{-4} \text{ sec.}^{-1}, \\ k_\beta &= k \frac{1}{K+1} = 1.570 \times 10^{-4} \text{ sec.}^{-1}, \end{aligned} \right\} T = 293.1^\circ \text{ K.}$$

$$\left. \begin{aligned} E_A^\alpha &= E_A + \Delta H \frac{1}{K+1} = 16,890 \text{ cals.}, \\ E_A^\beta &= E_A - \Delta H \frac{K}{K+1} = 17,050 \text{ cals.} \end{aligned} \right\} T = 298.1^\circ \text{ K.}$$

The analysis of data at other temperatures yields the relations

$$(k_\alpha/\eta) = 3.492 \times 10^{13} e^{-20910/RT}$$

and  $(k_\beta/\eta) = 7.877 \times 10^{13} e^{-21070/RT}.$

It is noteworthy that the inclusion of the small heat of reaction has caused the ratio of the pre-exponential factors to change from a value exceeding unity§ to one less than unity. When we compare either value with that afforded by the viscosity relationship, modified to account for the tendency of velocity to persist after collision (p. 10),

$$(k/\eta) = 3\pi r \left( \frac{1}{m_1} + \frac{1}{m_2} \right) e^{-E/RT}, \quad (7)$$

we find that more solute-solvent collisions take place than are necessary to explain the absolute rate of reaction. This significant result is applicable to the mutarotations of all reducing sugars. The second consequence of our analysis is that water, regarded as a solvent catalyst, now falls into line with solute catalysts (Chapter X), and the anomaly of a low rate of reaction attended by an apparently low energy of activation is removed.

The relative velocities of mutarotation in ordinary water and in

† Sturtevant, *J. Amer. Chem. Soc.*, **59**, 1528, (1937).

‡ Cf.  $\Delta H_{298.1} = -175$  calories, found by Rowe and Parks, *J. Chem. Physics*, **14**, 383, (1946).

§ *The Kinetics of Reactions in Solution*, 1st ed., p. 234, (1933).

heavy water ( $D_2O$ ) over a temperature range of  $30^\circ$  is† given by the equation

$$\frac{(k_{H_2O}/\eta_{H_2O})}{(k_{D_2O}/\eta_{D_2O})} = 1.64e^{510/RT}.$$

If the viscosity relationship sufficed to explain the difference in rates we would expect the first factor to be the inverse ratio of the reduced masses,  $\mu$ , since‡

$$\frac{(k_{H_2O}/\eta_{H_2O})}{(k_{D_2O}/\eta_{D_2O})} = \left(\frac{\mu_D}{\mu_H}\right)e^{(E_D - E_H)/RT}$$

and the molecular radii are the same. The calculated ratio of the reduced masses is 1.03 and the difference between the  $B$  terms calculated from the data of G. N. Lewis and Macdonald‡ is 520 calories. Thus it appears that the change in viscosity is only one of the factors concerned, and others, particularly the difference in residual energies, must play a part.

### *The Mutarotation of Aluminium Benzoylcamphor in Carbon Tetrachloride*

There is a well-known elementary ion which has a lethal biological effect in one electrovalent state and is innocuous in another. It is precisely this specificity in chemistry that accounts for much of its interest. Beryllium benzoylcamphor mutarotates slowly and in an uncomplicated manner in inert solvents; the corresponding aluminium compound mutarotates by a consecutive unimolecular mechanism.§ The specific optical rotation,  $\alpha_t$ , at time  $t$  is then related as follows to the initial and final rotations,  $\alpha_0$  and  $\alpha_\infty$ , and to the concentration,  $z$ , of product at time  $t$ :

$$\frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty} = \frac{a - z}{a} = \frac{k_1}{k_1 - k_2} e^{-k_2 t} - \frac{k_2}{k_1 - k_2} e^{-k_1 t}. \quad (8)$$

$k_1$  is the unimolecular constant for the first step and  $k_2$  the unimolecular constant for the second step:  $a$  is the initial concentration of solute (eqn. II (10)). The precision with which this equation reproduces the experimental facts is illustrated in one of the tables reproduced here from the work of Lowry and Traill (Table 4).

† Moelwyn-Hughes, Klar, and Bonhoeffer, *Z. physikal. Chem.*, **A**, **169**, 113, (1934).

‡ *J. Amer. Chem. Soc.*, **55**, 4730, (1933).

§ Lowry and Traill, *Proc. Roy. Soc. A*, **132**, 416, (1931).

We have analysed the complete data for the uncatalysed reaction, taking the inquiry a stage farther than was attempted by the investigators. Expressed in reciprocal seconds and  $\ln_e$ , as usual, we find

$$k_1 = 1.14 \times 10^{12} e^{-19000/RT}$$

and

$$k_2 = 2.50 \times 10^{14} e^{-22940/RT},$$

or, using the viscosity equation,

$$(k_1/\eta) = 6.86 \times 10^{15} \exp(-21375/RT)$$

and

$$(k_2/\eta) = 1.50 \times 10^{18} \exp(-25315/RT).$$

Table 4

*The Mutarotation of M/100 Aluminium Benzoylcamphor in Carbon Tetrachloride plus Pyridine at 20° C. ( $\lambda = 5,461 \text{ \AA.}$ )*

$$\alpha_t = 1244.5 - 867e^{-0.541t} + 258e^{-0.115t}.$$

$t$ (minutes)	$\alpha_t$ (observed)	$\alpha_t$ (calculated)	Difference (obs. — calc.)
0.9	962	933	+ 29
1.1	1,031	984	+ 47
1.7	1,100	1,106	- 6
2.1	1,159	1,164	- 5
2.3	1,200	1,190	+ 10
2.8	1,234	1,236	- 2
3.1	1,259.5	1,260.5	- 1
3.5	1,287.0	1,285.0	+ 2
4.0	1,301.0	1,306.0	- 5
4.5	1,319.0	1,320.5	- 1.5
4.9	1,327.0	1,328.0	- 1.0
5.3	1,333.5	1,334.0	- 0.5
5.8	1,338.0	1,338.0	0
6.2	1,340.0	1,339.5	+ 0.5
6.7	1,340.0	1,340.0	0
7.3	1,338.0	1,338.0	0
8.0	1,335.5	1,335.0	+ 0.5
8.5	1,332.0	1,332.0	0
9.2	1,326.0	1,327.5	- 1.5
10.1	1,322.5	1,321.0	+ 1.5
11.4	1,312.0	1,312.0	0
13.2	1,300.0	1,300.0	0
14.8	1,291.0	1,291.0	0
16.7	1,281.5	1,282.0	- 0.5
18.4	1,275.5	1,275.5	0
20.0	1,271.0	1,270.0	+ 1.0
23.7	1,261.0	1,261.0	0
29	1,253.5	1,253.5	0
37	1,247.5	1,248.0	- 0.5
51	1,245.0	1,245.0	0
$\infty$	1,244.5	—	—

Both  $k_1$  and  $k_2$  are, like all racemization constants, composite quantities, for which allowance must be made when comparing these experimental equations with equation (7). Comparison in the case of the first reaction requires that  $r = 9.25 \text{ \AA.}$ , which, though large, is not inconsistent with the voluminous structure of this solute, of molecular weight equal to 792 grams. When, however, we compare the rate of the second, and slower, reaction, with the theoretical formula, we find it to be greater than can be accounted for on the simple collisional basis. As we shall see in a later section, the participation of two internal degrees of freedom can adjust matters.

### *The Influence of the Solvent*

It would be indeed rash to conclude, because the rate of decomposition of nitrogen pentoxide and certain other molecules is mainly uninfluenced by their environment, that all unimolecular reactions follow suit. There are, in fact, definite indications to the contrary, and some unimolecular reactions in solution respond to their solvents in such a way as to suggest that they would not proceed by the same mechanism in the gaseous phase. The one truthful, though not very helpful, general statement that can be made is that the rate of unimolecular reactions in solution is a property specific to both solute and solvent.

We are sailing in those troubled waters where experimental evidence is our only guide. If there is a theory which could have predicted in advance that the rate of decomposition of nitrogen pentoxide would be speeded up in dichlorethane and slowed down in dichloropropane (see Table 1), it yet remains to be formulated. It is, therefore, to be much regretted that no substantial experimental contributions can be recorded in this field since the first edition of this work appeared. With one exception, the pioneer investigations of von Halban remain the major contribution. The explanation is not far to seek: it takes a single investigator about one year to prepare organic solvents in sufficient quantity and purity to enable him to examine the kinetics of one reaction. Traces of impurity in some solvents can alter the rate of decomposition a thousandfold. We must allow for this lack of uniformity when discussing the results of Table 5.

In attempting to trace the mechanism of the solvent effect, every clue, however slender, must be followed.

The apparent energy of activation of the decomposition of triethylsulphonium bromide seems to diminish as the dipole moment of the solvent increases.

Table 5

Reference	Reactant	Solvent	$E_A$	$\ln A$
(1)	Cis-azobenzene $\rightarrow$ trans-azobenzene	CCl <sub>4</sub>	23,200	26.06
(1)	" "	C <sub>6</sub> H <sub>6</sub>	23,400	26.04
(1)	" "	CH <sub>3</sub> COOH	23,000	25.17
(2)	Camphorcarboxylic acid	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	28,960	30.56
(2)	" "	H <sub>2</sub> O	29,640	30.02
(2)	" "	C <sub>6</sub> H <sub>6</sub>	27,800	28.88
(3)	Triethylsulphonium bromide	C <sub>6</sub> H <sub>11</sub> OH	33,140	37.84
(3)	" "	C <sub>3</sub> H <sub>7</sub> OH	33,120	36.87
(3)	" "	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	32,180	34.70
(3)	" "	CH <sub>3</sub> COOH	31,060	33.01
(3)	" "	CHCl <sub>3</sub>	33,010	41.57
(3)	" "	C <sub>2</sub> H <sub>5</sub> Cl <sub>4</sub>	30,350	37.70
(4)	" "	C <sub>3</sub> H <sub>7</sub> Cl <sub>4</sub>	30,410	37.87
(3)	" "	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	28,290	34.44
(4)	" "	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + x per cent. C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	28,870	35.14
(5)	" "	0	35,900	40.23
(5)	" "	25	34,800	39.41
(5)	" "	50	33,100	37.86
(5)	" "	75	32,700	38.56
(6)	Benzylhydroxytriazole-carboxylic acid ester	CHCl <sub>3</sub>	36,270	48.77
(6)	" "	C <sub>6</sub> H <sub>5</sub> OH	30,670	36.09
(6)	" "	(CH <sub>3</sub> ) <sub>2</sub> CO	29,000	35.46
(6)	" "	CH <sub>3</sub> OH	26,530	29.16
(7)	Acetonedicarboxylic acid	C <sub>6</sub> H <sub>5</sub> OH	26,600	37.54
(7)	" "	C <sub>3</sub> H <sub>7</sub> OH	25,800	37.26
(7)	" "	C <sub>4</sub> H <sub>9</sub> OH	23,200	32.25
(7)	" "	iso-C <sub>3</sub> H <sub>9</sub> OH	22,200	30.83
(7)	" "	iso-C <sub>6</sub> H <sub>11</sub> OH	22,100	30.63
(7)	" "	iso-C <sub>4</sub> H <sub>9</sub> OH	21,500	29.63
(7)	" "	HOH	23,200	32.29
(8)	Benzenediazonium chloride	HOH	27,030	36.01
(9)	" "	CH <sub>3</sub> OH	27,130	36.72
(9)	" "	C <sub>2</sub> H <sub>5</sub> OH	26,930	36.34
(9)	" "	C <sub>4</sub> H <sub>9</sub> OH	27,310	35.99
(9)	" "	iso-C <sub>4</sub> H <sub>9</sub> OH		
(9)	" "	CH <sub>3</sub> COOH		
(9)	" "	C <sub>6</sub> H <sub>5</sub> COOH		

Reference	Reactant	Solvent	$E_A$	$\ln A$
(10)	$\beta$ -Bromethylamine	$\begin{cases} \text{H}_2\text{O} \\ +x \text{ per cent.} \\ \text{CH}_3\text{OH} \end{cases}$		
			$x$	
			0	24,710
			25	19,920
			50	20,210
(11)	"		75	21,380
				25.80
(12)	Trichloracetic acid	$\text{C}_6\text{H}_5\text{N}$	28,350	33.82
(13)	" "	$\text{H}_2\text{O}$	37,050	45.00
(14)	Trinitrobenzoic acid	$\text{H}_2\text{O}$	29,970	32.85
(14)	" "	$\text{C}_6\text{H}_5\text{OCH}_3$	30,730	31.13
(14)	" "	$\text{C}_6\text{H}_5\text{NO}_2$	34,990	33.75
(14)	" "	$\text{C}_6\text{H}_5\text{COCH}_3$	25,450	24.23
(14)	" "	$\text{C}_6\text{H}_5\text{CH}_3$	31,600	27.68

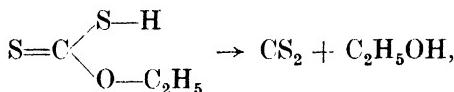
- (1) G. S. Hartley, *Trans. Chem. Soc.*, 633, (1938).
- (2) Bredig and Balcom, *Berichte*, **41**, 740, (1908); Fajans, *Z. physikal. Chem.*, **73**, 25, (1910).
- (3) von Halban, *ibid.*, **67**, 129, (1909).
- (4) Essex and Gelormini, *J. Amer. Chem. Soc.*, **48**, 882, (1926).
- (5) Corran, *Trans. Faraday Soc.*, **23**, 605, (1927).
- (6) Dimroth, *Annalen*, **373**, 367, (1910).
- (7) Wiig, *J. Physical Chem.*, **32**, 961, (1928); **34**, 596, (1930).
- (8) Brandsma, *Thesis*, Delft, (1925); see *Tables Annuelles*, (1930).
- (9) Pray, *J. Physical Chem.*, **30**, 1477, (1926).
- (10) Freundlich and Neumann, *Z. physikal. Chem.*, **87**, 69, (1914).
- (11) Freundlich and Kroepelin, *ibid.*, **122**, 39, (1926).
- (12) Goldschmidt and Bräuer, *Berichte*, **39**, 109, (1906).
- (13) Kappanna, *Z. physikal. Chem.*, **A**, **158**, 355, (1932).
- (14) Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **A**, **131**, 186, (1931).

On plotting the values of  $E_A$  for these reactions against a suitable function of the dielectric constant,  $D$ , such as  $[D+2(1-LT)]/3D$ , we find varying results. This factor happens to be the same for nitrobenzene and acetophenone, though the difference in apparent energy of activation for the decomposition of trinitrobenzoic acid in these solvents is 10 kilocalories. In decarboxylations, therefore, it would appear that electrostatic contributions to the energy of activation are not an important factor. A more regular dependence of the logarithm of the velocity coefficient on a function of the dielectric constant has been found in the mutarotation of glucose.<sup>†</sup>

Some slight regularity is to be discerned on introducing the viscosity correction, which has the effect of smoothing, but not of eliminating, the variation in the apparent critical increments. This

<sup>†</sup> Dyas and D. G. Hill, *J. Amer. Chem. Soc.*, **64**, 236, (1942); see also Magat, *Z. physikal. Chem.*, **A**, **162**, 432, (1932).

is apparent from the data cited in Table 5, from the early results (Table 6) of von Halban and Kirsch† on the reaction



and from the later work of (Miss) M. M. Jamison and E. E. Turner‡ on the mutarotation, in chloroform and in ethylalcoholic solution, of the cinchonidine salt of the *d*-form of N-benzoyl-4:6:4'-tribromo-diphenylamine-2-carboxylic acid. Without the viscosity correction, we have  $E_A = 19,700 \pm 1,500$  calories per mole; the corrected energies lie within the region  $22,000 \pm 500$ . In these reactions we must clearly allow for the fact that the rate at which activated molecules are produced is a function of the solvent in which they react.

*Table 6*  
*The Decomposition of Xanthogenic Acid in Various Solvents*

Solvent	$E_A$	$B$	$E$
$\text{C}_6\text{H}_5\text{NO}_2$	12,000	3,040	15,040
$\text{C}_6\text{H}_6$	13,790	2,850	16,640
$\text{CHCl}_3$	14,080	1,350	15,430
$\text{C}_6\text{H}_{14}$	14,600	1,660	16,260
$(\text{CH}_3)_2\text{CO}$	15,190	1,600	16,790
	$13,930 \pm 1,930$		$16,030 \pm 900$

### *The Molecular Statistics of Complicated Unimolecular Reactions*

The instances examined so far have been either decompositions of very simple molecules or elementary changes in more complex molecules; the agreement between calculated and observed velocity coefficients has justified our assumption that the rates of activation and reaction have been equal. When more complicated chemical changes are considered these two quantities need not be the same. For reactions of the true unimolecular type, the rate of activation, which still depends, of course, on the number of suitable collisions, is often considerably greater than, and does not determine, the velocity of reaction. The rate of chemical change is now governed by the frequency of interatomic vibrations, and by other factors, and cannot be evaluated without a fuller knowledge of the dynamics of activated

† *Z. physikal. Chem.*, **82**, 325, (1913).

‡ *Trans. Chem. Soc.*, **1646**, (1938).

molecules. The immediate problem is to account, on a collision mechanism, for a rate of activation great enough to sustain a sufficient fraction of the total number of molecules in an energized state. This becomes possible if the energy of activation is regarded as being distributed between a number of internal degrees of freedom of the reacting molecule. Adopting equations I(28) and I(57), the rate of production of activated molecules by collision becomes

$$\frac{dn}{dt} = n \frac{3\pi\eta\sigma}{2m} e^{-E/RT} \left(\frac{E}{RT}\right)^F \frac{1}{F!},$$

where  $F$  is one less than the total number of degrees of freedom involved. If this be equated to the observed rate of chemical change,  $dn/dt = kn$ , it becomes possible to evaluate the minimum number of degrees of freedom which must be concerned in the activation process:

$$k = \frac{3\pi\eta\sigma}{2m} e^{-E/RT} \left(\frac{E}{RT}\right)^F \frac{1}{F!}. \quad (9)$$

The values of  $F$  thus found for a number of unimolecular reactions in solution are given in Table 7. By applying the Arrhenius equation, we see that

$$E = E_A + B + FRT. \quad (10)$$

The observed critical increment ( $E_A$ ) and the corrected value ( $E_A + B$ ) have been determined by plotting the logarithm of  $k$  and of  $k/\eta$  respectively against  $1/T$ . On an average, each of these reactions has been investigated at five temperatures over a range of  $40^\circ$ , the actual temperatures having varied from  $0^\circ$  to  $140^\circ$ . With one or two exceptions, the energy of activation is considered to be accurate to within about  $\pm 500$  calories. The viscosity data have been taken from the *International Critical Tables*, vol. vii, 1930. The correction introduced into the critical increment by allowing for the temperature coefficient of the collision frequency depends not only on the solvent but also on the temperature at which the kinetic measurements were made, and varies from 880 calories for chloroform at  $40$ – $70^\circ$  to 5,680 calories for acetophenone at  $70$ – $140^\circ$ . The numbers in the last column of Table 7 are the nearest integers which will satisfy equation (9) when the observed velocity coefficients are substituted for  $k$ ;  $k_{\text{calc}}$  is the value assumed by  $k$  when this value of  $F$  is used in the same equation.

It will be seen from this table that the velocities of these reactions can be accounted for if a small number—from 1 to 7—of internal

Table 7

Reference	Reactant	Solvent	$E_A$	$E_A + B$	$v_{\text{eff}} \times 10^3$	$k_{\text{obs}}$		F
						Obs.	Calc.	
(1)	Triethylsulphonium bromide	PhNO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> Cl <sub>4</sub> CHCl <sub>3</sub> Pr <sup>a</sup> OH	28,290 30,350 33,010 33,120	31,340 33,180 33,890 37,000	10.94 9.90 4.50 9.16	2.11 × 10 <sup>-4</sup> 2.19 × 10 <sup>-4</sup> 2.07 × 10 <sup>-4</sup> 1.53 × 10 <sup>-4</sup>	2.96 × 10 <sup>-4</sup> 1.66 × 10 <sup>-4</sup> 9.84 × 10 <sup>-5</sup> 2.14 × 10 <sup>-4</sup>	4 6 7*
(2)	2:4:6-Trinitrobenzoic acid	CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> H <sub>2</sub> O PhCOMe	31,080 29,970 25,450	33,820 33,080 31,130	7.16 4.69 10.80	8.51 × 10 <sup>-7</sup> 3.33 × 10 <sup>-8</sup> 5.79 × 10 <sup>-7</sup>	5.43 × 10 <sup>-7</sup> 3.91 × 10 <sup>-8</sup> 4.39 × 10 <sup>-7</sup>	3 4 2
(3)	Camphorcarboxylic acid	PhCH <sub>3</sub> PhCOMe	31,600 28,900	33,620 32,020	3.80 10.80	1.62 × 10 <sup>-4</sup> 1.59 × 10 <sup>-4</sup>	4.20 × 10 <sup>-4</sup> 2.30 × 10 <sup>-4</sup>	1 3
(4)	Trichloracetic acid	H <sub>2</sub> O	29,640	32,690	4.69	3.31 × 10 <sup>-7</sup>	2.18 × 10 <sup>-7</sup>	2
(5)	Acetonedicarboxylic acid	PhNH <sub>2</sub> H <sub>2</sub> O	28,350 23,320	32,050 27,240	15.40 4.69	1.05 × 10 <sup>-4</sup> 5.48 × 10 <sup>-8</sup>	9.44 × 10 <sup>-5</sup> 2.05 × 10 <sup>-3</sup>	5 4
(6, 7)	Malonic acid	"	28,820	31,620	4.69	1.41 × 10 <sup>-7</sup>	2.11 × 10 <sup>-7</sup>	1
(7)	Allylmalonic acid	"	27,970	30,820	4.69	2.46 × 10 <sup>-7</sup>	5.03 × 10 <sup>-7</sup>	1
(7)	Diethylmalonic acid	"	33,430	36,250	4.69	2.00 × 10 <sup>-8</sup>	4.34 × 10 <sup>-8</sup>	4
(8)	Mesoxylic acid	"	33,700	36,330	4.69	1.82 × 10 <sup>-8</sup>	1.33 × 10 <sup>-8</sup>	3
(8)	Benzenediazonium chloride	"	23,360	27,110	4.69	3.43 × 10 <sup>-3</sup>	6.70 × 10 <sup>-3</sup>	3
(8)	<i>o</i> -Toluenediazonium chloride	"	23,440	27,310	4.69	8.97 × 10 <sup>-8</sup>	5.00 × 10 <sup>-8</sup>	3
(8)	<i>m</i> -Toluenediazonium chloride	"	22,800	26,070	4.69	8.89 × 10 <sup>-8</sup>	1.22 × 10 <sup>-8</sup>	3
(8)	<i>p</i> -Toluenediazonium chloride	"	27,680	31,150	4.69	5.20 × 10 <sup>-4</sup>	5.51 × 10 <sup>-4</sup>	5
(9)	Phenylbenzyl-methylallyl-ammonium bromide	CHCl <sub>3</sub>	29,960	31,620	4.50	1.04 × 10 <sup>-8</sup>	1.38 × 10 <sup>-8</sup>	7

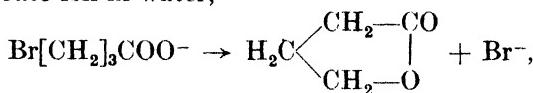
(1) von Halban, *Z. physikal. Chem.*, **67**, 129, (1909).(2) Moolwyn-Hughes and Hinselwood, *Proc. Roy. Soc., A*, **131**, 186, (1931).(3) Fajans, *Z. physikal. Chem.*, **73**, 25, (1910); also private communication from Professor Freudenberg.(4) Goldschmidt and Brüuer, *Berichte*, **39**, 109, (1906).(5) Wilg, *J. Physical Chem.*, **34**, 596, (1930); **32**, 961, (1928).(6) Bernoulli and Wege, *Helv. Chim. Acta*, **2**, 511, (1919).(7) Knaus, *Thesis*, Bâle, (1923); vide *Tables Annuelles*, (1928).(8) Cain and Nicoll, *Trans. Chem. Soc.*, **81**, 1412, (1902).(9) von Halban, *Berichte*, **41**, 2417, (1908).

degrees of freedom of the reacting molecules come into play during collisional activation. It should, however, be emphasized that these may not be the actual numbers involved; they are the minimum values which make it possible for the observed rate to be maintained. At the same time, it is not improbable that some of them represent the actual numbers of degrees of freedom which are operative. The number marked with an asterisk indicates both the minimum value of  $F$  which will account for the observed rate and the value of  $F$  which corresponds to the maximum rate of activation. In other words, if  $F$  were taken as 8,  $k_{\text{calc}}$  would be lower than that given in the table. Unless the collision term used is very much in error, it can therefore be concluded that 8 degrees of freedom in all come into play when triethylsulphonium bromide decomposes in chloroform solution.

The same analysis, applied to more recent data, furnishes similar figures. Thus, for example, the depolymerization of the dimeric form of nitroso-*iso*-propylacetone has been shown† to require, in benzene

† K. D. Anderson and Hammick, *Trans. Chem. Soc.*, **30**, (1935).

solution, a minimum value of  $F = 4$ . The lactonization of the  $\gamma$ -brombutyrate ion in water,



requires  $F = 7,\dagger$  and an intermediate figure is indicated for the decomposition of diphenyliodonium iodide in iodobenzene. $\ddagger$

The average value of  $F$  found necessary in the first fifteen unimolecular reactions to be examined in the gaseous phase is 5. Looked at from this angle, therefore, the parallelism between unimolecular reactions in the gas phase and in various solvents is well maintained; and this was the object of the analysis.

In the second place, it will be observed that for one and the same reaction in different solvents, the minimal number of degrees of freedom which must be invoked often varies from solvent to solvent. It has therefore been suggested $\S$  that the varying values of  $F$  from solvent to solvent may indicate in a quasi-quantitative manner the extent to which the solvent enters into partnership with the reactant for purposes of decomposition.

Many alternative theories, as we have seen, are possible and will have to be tested in due course. Provided the rate of activation exceeds that of reaction, the medium effect may be associated with the variable deactivating influence of the solvent molecules.

In Bradley's treatment of unimolecular reactions in solution $\parallel$  a more frequent vibration is to hand, and, in the ten examples selected by him from Table 7, it appears that no internal activation is necessary. This, we consider, is placing too much responsibility on a rapid oscillation. More satisfactory results are obtained by Wheeler's theory, $\ddagger\ddagger$  which furnishes values of  $F$  that are lower by 1 or 2 than those originally computed.

#### *Other Expressions for Unimolecular Velocity Coefficients*

Only classical formulae have so far been employed in our attempts to interpret the constant  $A$  of the Arrhenius equation when applied to unimolecular reactions,

$$k_1 = Ae^{-E_A/RT}. \quad \text{I (4)}$$

$\dagger$  Caldin and Wolfenden, *ibid.*, 1239, (1936).

$\ddagger$  Fletcher and Hinshelwood, *ibid.*, 596, (1935).

$\S$  Moelwyn-Hughes, *ibid.*, 106, (1932). Cf. Wynne-Jones and Eyring, *J. Chem. Physics*, 3, 492, (1935), who have independently drawn the same conclusion.

$\parallel$  *Trans. Chem. Soc.*, 1910, (1935).

$\ddagger\ddagger$  Equation VIII (16); *Proc. Indian Acad. Sci.*, 4, 291, (1936).

The quantum theory offers a much wider choice, among which are included the following:

$$A = kT/h \quad (\text{Herzfeld}), \dagger \quad (11)$$

$$A = E/h \quad (\text{Dushman}), \ddagger \quad (12)$$

$$A = \left( \frac{kT}{h} \frac{E}{\pi h} \right)^{\frac{1}{2}} \quad (\text{Rodebush}), \S \quad (13)$$

and

$$A = 4\pi \left( \frac{kT}{h} \frac{\epsilon_0}{3h} \right)^{\frac{1}{2}}. \quad \text{VIII (31)}$$

Herzfeld's expression, in many ways the most satisfactory, has been extensively adopted as a kind of basic frequency in gaseous systems. Before applying it to reactions in solution, let us first compare the numerical value of  $kT/h$  with the frequency of collisions according to the simple viscosity equation. The results (Table 8) obtained from

*Table 8*

*A Comparison of a Classical Method and a Quantal Method for computing the Arrhenius Term A in Liquids*

$t^\circ \text{ C.}$	$(3\pi\eta\sigma/2m)$ for $\text{CCl}_4$	$(3\pi\eta\sigma/2m)$ for $\text{H}_2\text{O}$	$kT/h$ for either
10	$12.83 \times 10^{12}$	$55.56 \times 10^{12}$	$5.93 \times 10^{12}$
40	8.56	27.88	6.55
70	6.22	17.42	7.14

the two formulae are of the same order of magnitude, and, in non-polar liquids, lie near together. They differ in that the Herzfeld frequency increases proportionately with the temperature, and is not specific, whereas the other decreases with a rise in temperature and is specific. The examination by Wynne-Jones and Eyring|| of many reactions in solution in the light of Herzfeld's equation,

$$k_1 = (kT/h)e^{-E/RT}, \quad (14)$$

has given a considerable stimulus to the subject in general. In applying it we note that

$$E_{\text{obs}} = E_A - RT \quad (15)$$

and that  $E_{\text{calc}} = E_A + RT \ln_e(kT/hA)$ . (16)

† *Annalen der Physik*, **59**, 635, (1919). The equation is derived in Appendix I.

‡ See W. C. McC. Lewis, *A System of Physical Chemistry*, 3rd ed., iii, p. 232, Longmans, (1924).

§ *J. Amer. Chem. Soc.*, **45**, 606, (1923).

|| *J. Chem. Physics*, **3**, 492, (1935).

The conversion of fused phenyl-benziminophenyl ether into benzoyl-diphenylamine† yields the results

$$E_{\text{obs}} = 41,700$$

and

$$E_{\text{calc}} = 40,800,$$

a very favourable comparison. At 60° C.,  $kT/h$  is nearly  $7 \times 10^{12}$  second<sup>-1</sup>, and  $\ln_e(kT/h)$  is thus about 29.6. With the exception of the isomerization of *iso*-stilbene in the gas phase and the decomposition of acetone dicarboxylic acid in *iso*-butyl alcohol solution, which fit in perfectly with the prediction of the simple equation,  $A$  differs from and is usually greater than  $kT/h$ . Wynne-Jones and Eyring‡ express the ratio  $k_{\text{calc}}/k_{\text{obs}}$  as  $\exp(\Delta S_c/R)$ .

An explanation of how an approximately constant value of  $A$  may arise in a series of homologous unimolecular decompositions has been offered by Pelzer.§

Dushman's proposed expression for the unimolecular velocity constant

$$k_1 = (E/h)e^{-E/RT}, \quad (17)$$

though usually regarded as empirical, may well be interpreted in terms of Heisenberg's principle of indeterminacy, according to which an exact determination of any energy involves an uncertainty in the time

$$\Delta\epsilon\Delta t \doteq h. \quad (18)$$

It is doubtful whether the whole of the activation energy may be regarded as an 'uncertainty' energy, related in this simple manner to the time interval,  $\Delta t$ , which must in any case be proportional to the reciprocal probability per second that an activated molecule shall decompose, but the form of the equation is correct, and it has some interesting consequences. When we examine the data of Table III (3), for example, we find the following empirical relationship between the constants of the Arrhenius equation, when  $E_A$  is expressed in kilocalcs./mole, and  $A$  in seconds<sup>-1</sup>:

$$dE_A/dA = 3.5 \times 10^{-14}.$$

According to Dushman's equation, we expect

$$\frac{dE_A}{dA} = \frac{N_0 h}{1000 J} = 9.5 \times 10^{-15},$$

which is of the same order of magnitude ( $N_0$ ,  $J$ , and  $h$  are the

† A. W. Chapman, *Trans. Chem. Soc.*, **127**, 1992, (1925).

‡ *Loc. cit.*

§ *Z. Elektrochem.*, **39**, 608, (1933).

constants of Avogadro, Joule, and Planck). On examining Hinshelwood's data on the decomposition of ethers, ketones, and aldehydes in the gaseous phase,† we find values of  $dE_A/dA$  ranging from  $3 \times 10^{-14}$  to  $6 \times 10^{-15}$ . Thus Dushman's equation, despite its obviously too great simplicity, accounts for the simultaneous trend in the same direction which is taken by the two constants of the Arrhenius equation, and is consistent with the belief that, all other things being equal, the more energy which a molecule possesses the greater is the likelihood of its losing it.‡

There are manifest computational difficulties in extending such arguments. On the whole, we conclude that the equation of Herzfeld is in closest concord with the facts, in that, when accurately measured unimolecular reactions are examined in homologous groups, the gradient  $d \ln E_A/d \ln A$  lies nearer to the value of zero implicit in his formula than to the values of 1 and 2 implied, respectively, in the formulae of Dushman and Rodebush.

This seems an appropriate place to refer to a proposed mechanism of activation,§ according to which the two constants of the Arrhenius equation are connected by means of the relation  $d \ln E_A/d \ln A = CE_A^{\frac{1}{2}}$ , where  $C$  has a value which is common for the series. A proportionality between  $\ln A$  and  $E_A^{-\frac{1}{2}}$  has been found for the formation of certain quaternary ammonium salts,|| the combination of cyclopentadiene and benzoquinone in various solvents,†† the decomposition of certain carboxylic acids,†† and the alkaline hydrolysis of certain lactones and phthalides. §§

### *The Influence of Substitution upon the Kinetics of Unimolecular Reactions*

This aspect of the subject has received very inadequate attention.

The introduction of a new group into a reactant molecule usually alters its reactivity, the magnitude of the effect being comparable for

† See *The Kinetics of Chemical Change in Gaseous Systems*, 3rd ed., Oxford, (1933).

‡ *Chem. Rev.*, **10**, 259, (1932).

§ Hinshelwood and Fairclough, 'The functional relation between the constants of the Arrhenius equation', *Trans. Chem. Soc.*, 1575, (1937).

|| Fairclough and Hinshelwood, *loc. cit.*

†† *Idem*, *ibid.*, 236, (1938).

†† Fairclough, *ibid.*, 1186, (1938). In view of an excessive claim that 'This is the most striking example of a correlated change in  $E_A$  and  $\ln A$  which has hitherto been observed', it seems necessary to point out that one of the  $E_A$  values upon which the claim is based is in error by 10,000 calories.

§§ Hegan and Wolfenden, *ibid.*, 508, (1939).

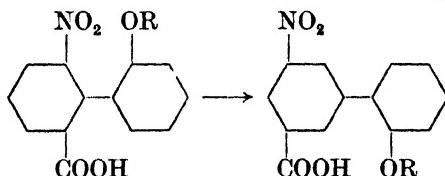
unimolecular and bimolecular reactions. The data in Table 9 have been compiled from the results of Knaus† and of Bernouilli and Wege‡ on the decomposition of substituted malonic acids, and may

Table 9

Acid	$E_A$	$\ln A$
Malonic	28,820	27.96
Diethylmalonic	33,430	32.99
Allylmalonic	27,970	27.20
Phenylmalonic	29,050	33.69
Mesoxalic	33,700	33.29

be compared with those which obtain, for example, in the bimolecular benzylation of amines in solution (p. 211). The substitution of a bromine atom for a hydrogen atom in camphorcarboxylic acid reduces the critical increment for the decomposition in acetophenone solution from 28,960 calories§ to 20,090 calories.|| On the other hand, the critical increments for the decomposition in water of *p*-bromobenzene-diazonium chloride†† and *p*-methylbenzenediazonium chloride†† are almost equal. As might be expected, the effect of substitution is a highly specific one.

The substitution of a dimethylamino group for the hydrogen atom in the *para* position of *cis*-diazobenzene causes no change in the apparent energy of activation.  $E_A$ , however, is about 1,800 calories greater when the substituent is the trimethylammonium ion, §§ but some of this difference may be due to a necessary change in solvent. The introduction of methyl, ethyl, and *iso*-propyl radicals into the 2'-etheric position of 2-nitro-6-carboxy-2'-alkoxydiphenyl similarly has no pronounced effect on the apparent energy of activation



† *Thesis*, Bâle, (1923); *Tables Annuelles*, (1928).

‡ *Helv. Chim. Acta*, **2**, 511, (1919); see also Burk and Daus, *J. Physical Chem.*, **35**, 1461, (1931); Dinglinger and Schröer, *Z. physikal. Chem.*, **A**, **179**, 401, (1937).

§ Fajans, *ibid.*, **73**, 25, (1910).

|| Creighton, *ibid.*, **81**, 543, (1913).

†† 27,000 calories; Euler, *Annalen*, **325**, 292, (1902).

‡‡ 27,680 calories, Cain and Nicoll, *Trans. Chem. Soc.*, **81**, 1412, (1902).

§§ G. S. Hartley, *ibid.*, **633**, (1938).

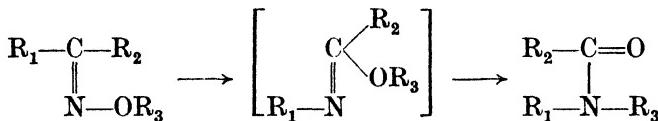
required for the racemization in ethylalcoholic solution.<sup>†</sup> It is possible, however, that small energy changes occur but cannot be detected. As the results stand at present, the  $A$  terms appear to fall regularly in the order cited. More marked changes are apparent<sup>‡</sup> in the effect of double substitution on the rate of decomposition, in aqueous solution, of the aminoethylsulphonate ion (Table 10).

Table 10

*Constitutive Effects on the Kinetics of the Reaction*

$R_2$	$E_A$ (calories/gm. mole)	$A \times 10^{-18}$ (sec. <sup>-1</sup> )
N-piperidyl	23,830	9.85
Dimethyl	23,470	9.84
Diethyl	23,680	7.46
Di-n-propyl	22,030	8.04
Diethanol	19,440	1.73
Phenylmethyl	18,500	0.34

The clearest demonstration of the effect of substituents on the kinetics of unimolecular reactions is to be found in the work of A. W. Chapman<sup>§</sup> on the Beckmann transformation of ketoximes in carbon tetrachloride solution:



Let us confine our attention to his results on the picryl ethers, for which  $\text{R}_3$  is 2:4:6-C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>. When  $\text{R}_2$  is the *p*-nitrophenyl group, the oxime is not readily isomerized; when  $\text{R}_2$  is the *p*-anisyl radical, a very rapid rearrangement takes place. Measurable velocities obtain with other substituents, and the results show that substitutions into the groups  $\text{R}_1$  and  $\text{R}_2$  make additive contributions to the energy of activation. Some figures illustrating Chapman's conclusion are to be found in Table 11, in which the energies have been corrected for the viscosity of the solvent.

An interesting series of homologous unimolecular reactions is provided by the ring closure, in aqueous alkaline solution, of straight-

<sup>†</sup> Li and Adams, *J. Amer. Chem. Soc.*, **57**, 1565, (1935).

<sup>‡</sup> T. D. Stewart and W. E. Bradley, *ibid.*, **54**, 1483, (1932).

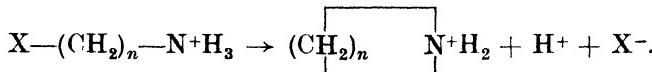
<sup>§</sup> *Trans. Chem. Soc.*, **448**, (1936).

Table 11

*The Effect of Substitution on the Energy of Activation of the Beckmann Isomerism of certain Ketoxime Picryl Ethers in Carbon Tetrachloride Solution*

$R_1$	$R_2$	$E$ (kilocalcs./gm. mole)	$\Delta E = E_s - E_u$
$C_6H_5$	$C_6H_5$	29.2	0
$C_6H_5$	$p\text{-}C_6H_4Cl$	30.8	+1.6
$p\text{-}C_6H_4Cl$	$C_6H_5$	29.8	+0.6
$p\text{-}C_6H_4Cl$	$p\text{-}C_6H_4Cl$	31.5	+2.3
$C_6H_5$	$p\text{-}C_6H_4CH_3$	26.5	-2.7
$p\text{-}C_6H_4CH_3$	$C_6H_5$	28.3	-0.9
$p\text{-}C_6H_4CH_3$	$p\text{-}C_6H_4CH_3$	25.8	-3.6

chained aliphatic aminoalkyl halides, containing the substituted groups at the molecular extremities:



Here X stands for a halogen atom and n is an integer. Thus, for example, the conversion of  $\epsilon$ -chloramylamine into piperidine hydrochloride corresponds to X = Cl and n = 5. Some results for typical members of this series are summarized in Table 12. Latterly, chains

Table 12

*Arrhenius Constants for certain Cyclization Reactions in Aqueous Alkaline Solution*

X	n	$E_A$ (kilocalcs./gm. mole)	$\ln_e A$ (sec. $^{-1}$ )
Br	2	24.9	34.7†
Br	3	22.3	26.1‡
Cl	4	19.8	30.8§
Cl	5	20.7	26.0

† Freundlich and Neumann, *Z. physikal. Chem.*, **87**, 69, (1914).

‡ Freundlich and Kroepelin, *ibid.*, **122**, 39, (1926).

§ Freundlich and Salomon, *Berichte*, **66**, 355, (1933).

|| Salomon, *Helv. Chim. Acta*, **19**, 743, (1936).

containing as many as seventeen methylene groups have been investigated,† some of them in various solvents. Salomon‡ has examined the energies of activation to discover what fraction may be represented by the energy of buckling, which it is not difficult to estimate

† Salomon, *Helv. Chim. Acta*, **19**, 743 (1936).

‡ *Trans. Faraday Soc.*, **32**, 153, (1936).

if one adopts Langmuir's hypothesis. The rates of reaction generally differ in the way which we would expect if allowance is made for the difference in energy of the straight and coiled patterns of the aliphatic compounds, and there seems, on the whole, little doubt that Salomon's approach is along the right lines.

We naturally expect the influence of substituents on pseudo-unimolecular reactions to follow that found when the change takes place between the reactants at comparable concentrations in a solvent, and in this we are not disappointed when we compare the results discussed in Chapter VII with those given in Table 13, which

Table 13

*The Influence of Substitution on the Pseudo-unimolecular Alcoholysis of Acid Chlorides and of Methyl Chlorides in 60:40 Ether-Alcohol Solution*

	$E_A$ (cals./gm. mole)	$\log_{10} A$ (sec. <sup>-1</sup> )
Acid chloride:		
Acetyl	12,500	7·4
<i>p</i> -NO <sub>2</sub> -benzoyl	11,100	5·5
<i>p</i> -Br-benzoyl	13,450	6·2
<i>p</i> -Cl-benzoyl	13,850	6·5
<i>p</i> -I-benzoyl	13,450	6·2
<i>p</i> -F-benzoyl	14,650	7·8
Benzoyl	14,400	6·6
<i>p</i> -CH <sub>3</sub> -benzoyl	15,900	7·5
<i>p</i> -CH <sub>3</sub> O-benzoyl	18,650	9·4
Methyl chloride:		
Diphenyl	26,650 (?)	13·47 (?)
Triphenyl	13,420	7·94
<i>p</i> -Tolylidiphenyl	12,450	7·82
<i>p</i> -F-triphenyl	13,560	7·92
<i>p</i> -Cl-triphenyl	13,480	7·23
<i>p</i> -Br-triphenyl	14,050	7·83
<i>p</i> -I-triphenyl	13,190	7·30
<i>p</i> -NO <sub>2</sub> -triphenyl	16,710	8·38
$\alpha$ -Naphthyldiphenyl	13,010	7·74
$\beta$ -Naphthyldiphenyl	13,010	7·84

are taken from the papers of Branch and Nixon† and Nixon and Branch.‡ It would ill behove us, at this early stage in the development of the subject, to pursue the substitution theme any farther. We may, however, fully endorse the conclusion of these investigators

† *J. Amer. Chem. Soc.*, **58**, 2499, (1936).

‡ *Ibid.*, **58**, 492, (1936); see also Ward, *Trans. Chem. Soc.*, 2285, (1927); Norris and Morton, *J. Amer. Chem. Soc.*, **50**, 1795, (1928).

that 'no explanation of the effects of groups on the rates of alcoholysis of arylmethylchlorides can be both simple and complete'.

### *The Influence of Dilution upon the Kinetics of Unimolecular Reactions*

More than a hint as to the influence of solute concentration on the rate of unimolecular reactions in solution is given by equation (1), from an inspection of which we readily see that a change in the concentration may cause an increase, a decrease, or neither. Experiments show that very often the unimolecular velocity coefficient is quite unaffected by changes in dilution, and that, when a dilution effect is found, it is in the sense that an increase in the concentration of solute causes a decrease in the velocity. We therefore infer that, in general, deactivation by solute molecules is a more likely factor than subsidiary activation by binary collisions between solute molecules. Few experiments, however, have been carried out with sufficient care to justify a detailed analysis.

The pseudo-unimolecular velocity coefficients for the alcoholysis of triphenylchlormethane in ether-alcohol solution of the composition quoted† can, with a slight adjustment in form and units, be summarized as follows,

$$k = 6 \cdot 82 \times 10^7 \left( \frac{4 \cdot 1 + 10^4 c}{1 \cdot 4 + 10^4 c} \right) e^{-13420/RT},$$

in conformity with equation (1). Here  $c$  is the concentration of solute in gram moles per litre, and the equation refers to dilutions exceeding 1,000 litres per mole.

It is not yet possible to say how far equation (1), when systematically applied, as in the present work, can account for the concentration effect in stronger solutions. On integration, we obtain

$$\left( \frac{k_3}{k_1 k_5} + \frac{1}{k_1 s} \right) \ln \frac{c_0}{c_t} - \left( \frac{k_3}{k_1 k_5} + \frac{1}{k_1 s} - \frac{k_4}{k_2 k_5} \right) \ln \left( \frac{k_1 s + k_2 c_0}{k_1 s + k_2 c_t} \right) = t, \quad (19)$$

from which we see that the observed unimolecular constant,  $k$ , in the absence of solvent ( $s = 0$ ,  $k_1 = 0$ , and  $k_3 = 0$ ), is the high-concentration coefficient

$$k = \frac{1}{t} \ln \frac{c_0}{c_t} = \frac{k_4}{k_2 k_5}, \quad (20)$$

while the value corresponding to infinite dilution ( $k_2 = 0$ ) is

$$k = \frac{1}{t} \ln \frac{c_0}{c_t} = \frac{k_1 k_5 s}{k_5 + k_3 s}. \quad (21)$$

† Nixon and Branch, *ibid.*, **58**, 492, (1936).

Before the complete change from the pure liquid solute phase to the pure liquid solvent phase can be kinetically encompassed we must possess more knowledge than we now do of the properties of mixed liquids in the relatively simple systems which are free from temporal change. In the meantime, we proceed by experiment.

Kappanna† has made an interesting attempt to decipher his results on the rate of decomposition of trichloracetic acid in water at 80° C. Some of his data are given in Table 14, to which have been added molar fractions computed from the densities of the solutions. He

Table 14

*The Influence of Concentration on the Rate of Decomposition of Trichloracetic Acid in Water at 80° C.*

[CCl <sub>3</sub> .COOH] (moles/litre)	$k \times 10^6$ (minute <sup>-1</sup> ; log <sub>10</sub> )	Density (gm./c.c.)	[H <sub>2</sub> O] (moles/litre)	N <sub>s</sub> (mol. frac- tion of solvent)
0	183.5	0.972	54.00	1.000
0.25	156.6	0.988	52.61	0.995
0.50	136.9	1.007	51.40	0.990
1.00	98.5	1.043	48.87	0.980
2.00	51.0	1.1105	43.49	0.954
3.00	24.8	1.1800	38.33	0.927
4.00	10.1	1.2475	33.00	0.892
5.00	3.45	1.3150	27.68	0.847

regards water as participating in the reaction in the *n*th order so that the rate of decomposition of the acid becomes

$$-\frac{dc_a}{dt} = k_n c_a c_w^n.$$

Then

$$k = k_n c_w^n. \quad (22)$$

On plotting the logarithm of the observed velocity coefficient, *k*, against the logarithm of the concentration, *c<sub>w</sub>*, of water, it is found that *n* = 6. The reaction then appears to be a seventh-order one, indicating that in the rate-determining step one molecule of solute is simultaneously attacked by six molecules of solvent. This is a conclusion of very considerable interest, particularly in view of the apparent unimolecularity, in aqueous solution, of such reactions as



and



† *Z. physikal. Chem., A*, **158**, 355, (1932).

the kinetic data of which† may be summarized by the respective equations

$$\ln_e k = 29.9 - 19160/RT$$

and

$$\ln_e k = 36.0 - 27530/RT.$$

It has an obvious bearing also on all hydrolytic reactions and was, in fact, first obtained in connexion with them. Scatchard,‡ from an analysis of the kinetic data of Lewis and his collaborators§ on the inversion of cane sugar, estimated  $n$  as  $6 \pm 1$ . There are, however, other explanations of the effect, and Kappanna's conclusion may well prove to be more apposite to hydrolysis than to the reaction examined by him. The explanation offered by equation (1) is not, as can readily be shown, applicable in the present case. The role of ionization has, of course, been fully examined and found to be equally inadequate.

On account of the high concentrations involved, let us see how far an equation of the form

$$k = k_0 + (k_s - k_0)N_s^n \quad (23)$$

will take us,  $N_s$  being the molar fraction of solvent, and the constants  $k_0$  and  $k_s$  simply the unimolecular velocity constants for the decomposition of the solute in the fused and infinitely dilute states. We now find that  $n$  is 16 and that there is an unwarrantably great difference between  $k_0$  and  $k_s$ . No great gain has therefore resulted from the reformulation.

A more satisfactory expression for the dilution effect is

$$k = k_0 e^{-Kc/RT}. \quad (24)$$

With  $c$  in the units of gram molecules per litre and  $RT$  expressed in calories,  $K$  for the trichloracetic acid decomposition can be shown to have the numerical value of 55. The true coefficient of  $c$  in this expression, must, however, be a function of the molar composition and also of the dielectric constant if the energy of activation contains an electrostatic component.

Let us now consider the slightly more difficult case of a solute,  $A$ , in a solvent composed of two components,  $B$  and  $C$ , with both of which it reacts pseudo-unimolecularly. If the specific constants were

† Huddleston and Bassett, *Trans. Chem. Soc.*, **119**, 403, (1921); Green and Masson, *ibid.*, **97**, 2083, (1910).

‡ *J. Amer. Chem. Soc.*, **43**, 2387, (1921).

§ C. M. Jones and W. C. McC. Lewis, *Trans. Chem. Soc.*, **117**, 1120, (1920); Moran and Lewis, *ibid.*, **121**, 1613, (1922).

to be independent of the composition, we should have, in terms of molar fractions,  $N$ , the rate law

$$-\frac{dN_A}{dt} = k_{AB} N_A N_B + k_{AC} N_A N_C.$$

Hence the pseudo-unimolecular constant,  $k$ , which is independent of the unit of concentration (equation II(20)), becomes

$$k = k_{AB} N_B + k_{AC} N_C. \quad (25)$$

Moreover, if we confine attention to solutions containing but little solute, we have  $N_C = 1 - N_B$  very nearly, so that

$$k = k_{AC} + (k_{AB} - k_{AC})N_B, \quad (26)$$

which reduces, for solutions obeying Raoult's law, to

$$k = k_{AC} + (k_{AB} - k_{AC}) \frac{p_B}{p_B^0}. \quad (27)$$

An equation of this form has been found to apply to the simultaneous hydrolysis and alcoholysis of tertiary butyl chloride.†

### *Empirical Relations*

The variety of chemical changes and the range of conditions under which they occur make possible an almost unlimited diversity of kinetic phenomena. In the nature of things, it is therefore unlikely that any simple mathematical relation can describe more than a limited number of reactions. The restricted applicability of the theoretical equations which are used in this book has been repeatedly emphasized and need be stressed no further. Similarly confined in scope are the empirical formulae which have from time to time been advanced and may be considered briefly here.

Most of the attempts have been directed at correlating the two constants  $A$  and  $E_A$  of the Arrhenius equation.‡ Many of the equations can be expressed in the general form

$$k = K e^{E/Q} e^{-E/RT}. \quad (28)$$

The hydrolysis of sugars and glycosides by acids conforms to an equation of this type,  $K$  being unity and  $Q$  being a constant dependent upon the type of glycoside; for glucosides,  $Q = 857$  calories; for fructosides,  $Q = 743$  calories. All the members of one group are thus

† Olson and Halford, *J. Amer. Chem. Soc.*, **59**, 2644, (1937).

‡ See, for example, Boeseken, *Rec. trav. chim. Pays-bas*, **46**, 574, (1927); Gapon, *Ukraine Chem. J.*, **5**, 169, (1930).

hydrolysed at unit rate ( $k = 1$ ) at the same temperature, which is equal to  $Q/R$ .†  $K$  is also unity for some unimolecular reactions.‡ The kinetics of the decomposition of alcohols at the surface of solids are given by the same relation,  $Q$  now being a constant for a group of similarly constituted catalysts.§ It has been suggested that  $Q$  in the case of bimolecular reactions in solution is a function of the solvent.|| Another generalization, originally intended only for bimolecular reactions between amines and halides, is

$$\begin{aligned} E_A &= E + RT \ln(A/Z) \\ &= E + RT \ln P. \end{aligned} \quad (29)$$

For a series of reactions having a common energy of activation, we have††

$$\frac{dE_A}{d \ln P} = RT. \quad (30)$$

Even a cursory glance at the literature since 1932 shows that this relationship has a much wider range of applicability than was originally thought.†† With the growth of the subject other empirical formulae will unquestionably appear. For example, the velocity of decomposition of a number of different carboxylic acids in water is given with fair accuracy by the general equation

$$k = 2.3 \times 10^{14} \times e^{-E/RT},$$

as the results given in Table 15 indicate. When dealing with unimolecular reactions, a constancy in  $A$  is seldom found accompanied by such a wide variation in  $E_A$ , and may indicate a common interatomic frequency characteristic of the carboxyl group. §§ At present,

Table 15

Acid	$E_A$	$\ln A$
Mesoxalic	33,700	33.3
Diethylmalonic	33,430	33.0
Trinitrobenzoic	29,970	32.9
Phenylmalonic	29,050	33.7
Acetonedicarboxylic	23,200	32.3

† Moelwyn-Hughes, *Thesis*, Liverpool, p. 88, (1928).

‡ Syrkin, *Z. anorg. Chem.*, **199**, 28, (1931).

§ G. M. Schwab, *Z. physikal. Chem.*, **B**, **5**, 406, (1929).

|| Holdzschmidt, *Z. anorg. Chem.*, **200**, 82, (1931).

†† Cf.  $dE_A/d \ln A = RT(1 - T/L)$  obtained in Chapter IV.

‡‡ *Chem. Rev.*, **10**, 240, (1932).

§§ Cf. Polanyi and Wigner, *Z. physikal. Chem.*, 'Haber-Band', 439, (1928).

however, it is wisest to recall the facts that the equation is quite empirical and of a strictly limited applicability. Like the other empirical relations discussed here, its immediate value lies in its utility and suggestiveness.

### *The Influence of Temperature on the Kinetics of Unimolecular Reactions*

Those unimolecular reactions which have been examined carefully and over extensive temperature ranges in solution conflict with the equation of Arrhenius, and are, as we have seen (p. 67), more consonant with the equation

$$k = BT^{C/R}e^{-E/RT}. \quad \text{I (6)}$$

In such cases the search for a relationship between the 'constants' of the Arrhenius equation is pointless, as neither  $A$  nor  $E_A$  is, in fact, a constant. On the evidence available we infer that all unimolecular reactions in solution will ultimately be found to conform more closely to equation I (6) than to the Arrhenius equation.

The interpretation of this experimental formula is not difficult.  $C$ , as Trautz points out (p. 4), is the difference between the specific heats of the reactive and the ordinary molecules. Experiment shows  $C$  to have a negative value (Table II (20)); hence, in general, the specific heat of the active molecule is less than that of a normal molecule. This, in turn, denotes a firmer binding of the molecular parts in the active molecule, so that complicated activation means a loosening of one bond at the expense of a tightening in other bonds.

The term  $B$  has, of course, the dimensions of a frequency. It is not, however, a pure frequency, such as  $\nu$  or  $kT/h$ , as early applications of the quantum theory to very simple unimolecular reactions led one to suppose, but a mean frequency, indicating a chord rather than a note, and of a form which is discussed in Appendix I.

## X

## CATALYSED REACTIONS

ANY substance which hastens a chemical reaction while retaining its identity is termed a catalyst. It may perform its work in a variety of ways: for example, by initiating reaction chains or lengthening previously existing ones, by increasing the concentration of molecules of one reactant in the locality of a molecule of the other, and by lowering the energy of activation. The last of these mechanisms is by far the commonest, although a few chain reactions in solution are known. The way in which ions of one sign congregate round those of the opposite sign, and the manner in which this clustering is altered by the addition of electrolytes and non-electrolytes have been described in Chapter IV. We are thus left with the task of discovering to what extent, and why, the energy of activation of any reaction is lowered by the presence of a catalyst. Experiment gives a direct answer to the first of these questions, and shows that the fall in the critical increment of any reaction is characteristic of the catalyst but independent of its amount. The second query goes to the root of the matter but finds no ready answer although shrewd guesses are being made. In a sense it is still true to say that the term catalysis is synonymous with unsolved mechanism.

In the presence of the catalyst, the uncatalysed and the catalysed reactions proceed simultaneously, so that  $k = k_0 + k_c[\text{catalyst}]^n$ . If successive additions of the catalyst bring about proportionate increases in the observed velocity,  $n$  is unity, and  $k_c$  becomes a bimolecular constant or catalytic coefficient. By plotting  $\ln k_c$  against  $1/T$  in the usual way, we can evaluate the critical increment of the catalytic reaction. It has already been stressed, and must be repeated here, that the value of  $E$  obtained from the equation

$$E = RT^2 \frac{d \ln k}{dT}$$

is often meaningless. If, as not infrequently it happens, even small amounts of catalyst produce a large effect on the velocity,  $k_0$  may be ignored in comparison with  $k_c$ . This is the case with the decomposition of hydrogen peroxide; in the presence of minute quantities of certain catalysts the unimolecular velocity constant is millions of

times greater than the constant for the uncatalysed decomposition. Occasionally, as with the hydrolysis of casein, the spontaneous reaction has never been detected under any conditions, and  $k_0$  accordingly does not enter. On the other hand, the two constants of the reaction may be commensurate: when this is so, a careful analysis of the influence of varying amounts of the catalysts is essential at all temperatures. A case in point is the decomposition of acetonedicarboxylic acid;  $k_0$  at 60° C. is  $5.48 \times 10^{-2}$  seconds<sup>-1</sup>; the addition of 0.0165 gram mole of aniline per litre gives

$$k = 11.9 \times 10^{-2}.$$

$k_c$  thus becomes 3.89 litres/gram molecule-second. On analysing the remaining data of Wiig in the same way, we find an energy of activation of about 13,900 calories for the catalysed reaction, which is 9,300 calories less than the value for the uncatalysed reaction. Aniline depresses by a similar amount (8,700 calories) the energy required for the decomposition of trichloracetic acid. Further examples are furnished in Table 1, from which we see that catalysts are as varied as the reactions which they facilitate and the media in which the chemical changes take place. Solute and solvent may both act as catalysts.

There are three criteria of thermal catalysis. The first criterion is the reduction by unity of the apparent order of reaction (p. 48). The second is the reduction in the apparent energy of activation. The third criterion, which is a fairly general though perhaps not a universal one, is that the catalytic coefficient belongs to the category of normal reactions, for which there is unit efficiency of activating collisions involving no internal degrees of freedom. This last conclusion is based on the detailed statistical analyses carried out by Polissar (reaction 15), Hinshelwood (reaction 16 and others like it), J. B. S. Haldane (reaction 4), Chapman (reaction 14), and Moelwyn-Hughes (reactions 5, 7, and 13).

The examples of catalysis selected for study in this chapter are those in which the uncatalysed change is a unimolecular one and for which the catalytic integer is 1. We then have

$$-\frac{dn_A}{dt} = k_1 n_A + k_2 n_A n_C, \quad (1)$$

where  $n_A$  is the concentration of the substance undergoing change, and  $n_C$  is the concentration of the catalyst. The observed unimolecular

Table 1

Reference	Reaction	Catalyst	$E_A$
(1)	The decomposition of hydrogen peroxide in aqueous solution	None	18,000
(2)		Iodide ion	13,500
(3)		Colloidal platinum	11,700
(4)		Liver catalase	5,500
(5)	The decomposition of acetone-dicarboxylic acid in aqueous solution	None	23,200
		Aniline	13,900
(6)	The hydrolysis of sucrose in aqueous solution	Hydrogen ion	25,560
(7)		Saccharase	8,700
(8)	The hydrolysis of casein in aqueous solution	Hydrochloric acid	20,600
(9)		Trypsin-kinase	14,400
(10)	The decomposition of triethyl-sulphonium bromide in acetone solution	None	33,500
		4 per cent. water	30,700
(11)	The decomposition of trinitrobenzoic acid in nitrobenzene solution	None	35,000
		Adventitious impurity, probably water	21,700
(12)	The decomposition of trichloroacetic acid	Water (solvent)	37,050
(13)		Aniline (solvent)	28,350
(14)	The Beckmann rearrangement of the picryl ether of benzophenone oxime in carbon tetrachloride solution	None	30,250
		Nitromethane	23,800
(15)	The decomposition of ethylene iodide in the gas phase and in carbon tetrachloride solution	None	37,000
		Iodine (atomic)	12,500
(16)	The decomposition of diethyl-ether in the gas phase	None	53,500
		Iodine (molecular)	34,300

- (1) Possibly some decomposition upon dust particles. Pana, *Trans. Faraday Soc.*, **24**, 486, (1928).
- (2) Walton, *Z. physikal. Chem.*, **47**, 185, (1904).
- (3) Bredig and von Berneck, *ibid.*, **31**, 258, (1899).
- (4) Williams, *J. General Physiol.*, **11**, 309, (1928).
- (5) Wiig, *J. Physical Chem.*, **32**, 961, (1928).
- (6) Lamble and Lewis, *Trans. Chem. Soc.*, **105**, 2330, (1914).
- (7) Nelson and Bloomfield, *J. Amer. Chem. Soc.*, **46**, 1025, (1924).
- (8) Nasset and Greenberg, *ibid.*, **51**, 836, (1929).
- (9) Moelwyn-Hughes, Pace, and Lewis, *J. General Physiol.*, **13**, 323, (1930).
- (10) von Halban, *Z. physikal. Chem.*, **67**, 129, (1909).
- (11) Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc., A*, **131**, 186, (1931).
- (12) Kappanna, *Z. physikal. Chem.*, **A**, **158**, 355, (1932); P. Johnson and Moelwyn-Hughes, *Proc. Roy. Soc., A*, **175**, 118, (1940).
- (13) Goldschmidt and Bräuer, *Berichte*, **39**, 109, (1906).
- (14) A. W. Chapman, *Trans. Chem. Soc.*, 1550, (1934).
- (15) Polissar, *J. Amer. Chem. Soc.*, **52**, 956, (1930); Arnold and Kistiakowsky, *J. Chem. Physics*, **1**, 166, (1933). See erratum added later.
- (16) Clusius and Hinshelwood, *Proc. Roy. Soc., A*, **128**, 82, (1930).
- (4, 7, 9) These figures refer to the optimum pH.

constant is thus linearly related to the concentration of catalyst, since

$$k = k_1 + k_2 n_C. \quad (2)$$

Now let us suppose that the true energy of activation in each case involves a distribution among internal degrees of freedom, so that, as in equation I (58),

$$E_1 = (E_A)_1 + F_1 RT$$

and

$$E_2 = (E_A)_2 + F_2 RT.$$

On the strength of the various statistical analyses referred to, we venture to assume that  $F_2$  is usually zero; hence

$$(E_A)_1 - (E_A)_2 = E_1 - E_2 - F_1 RT. \quad (3)$$

The difference between the apparent energies of activation of the uncatalysed and the catalysed reactions may thus denote a difference in the true energies of activation, or a positive value of  $F_1$ , or both. In many of the reactions under discussion, it is known that  $F_1$  has a positive value, but we cannot always be sure that the whole effect of the catalyst is to reduce the number of the degrees of freedom among which the energy of activation is shared (cf. the values of  $F$  given in Tables IX (7) and X (12)). If this were so, the role of the catalyst in thermal reactions would be, as Hinshelwood and Clusius have put it, to bring 'a smaller amount of energy to a point in the molecule where it is more effectively and economically utilized'.

The field in which we are searching is thus being narrowed down, but, despite a variety of theories of the nature of catalysis,† we are still a long way from discovering why certain molecules or ions are catalytic while others which closely resemble them are not.

Hydrogen ion is the arch-catalyst, and renewed interest in it has arisen since it was shown that the catalytic coefficients for the enolization of ketones and the mutarotation of sugars are normal bimolecular constants.‡ It is nevertheless appreciated that reactions which are hastened by hydrogen ion or by hydroxyl ion in aqueous solution must constitute a highly specialized type of catalysis, since the solvent, being amphoteric, can supply both ions. Moreover, in hydrolytic changes, the solvent participates stoichiometrically in the

† See, for example, Schochowitzky, *Acta Physicochim. U.S.S.R.*, **1**, 901, (1935); Horiuti and Polanyi, *ibid.*, **2**, 505, (1935); Rideal and H. S. Taylor, *Catalysis in Theory and Practice*, 2nd ed., Macmillan, (1926); G. M. Schwab (trans. by H. S. Taylor and R. Spence), *Catalysis from the Standpoint of Chemical Kinetics*, Macmillan, (1937).

‡ *Phil. Mag.*, **14**, 112, (1932).

reaction. A cautious attitude must accordingly be maintained towards conclusions based upon the study of these reactions when they are made the grounds of a theory which claims to be true for catalysis in general.

The literature upon catalysis in solution has attained such alarming proportions that only a very brief sketch can be given here. A few of the most important reactions may be dealt with in some detail.

#### *The Catalytic Mutarotation of Beryllium Benzoylcamphor in Non-Aqueous Solvents*

Lowry and Traill† have determined polarimetrically the velocity of the mutarotation of beryllium benzoylcamphor under the influence of various catalysts in carbon tetrachloride solution and in chloroform solution. A relatively slow unimolecular change is observed in pure carbon tetrachloride,  $k$  being  $6.66 \times 10^{-6}$  seconds $^{-1}$  at 25° C. In pure chloroform also there is some change, but its velocity is not accurately reproducible. Sometimes the reaction is completely arrested for a period of 1·2 hours. The authors interpret this as showing that mutarotation is not spontaneous, but must be aided by a catalyst, which is possibly a trace of impurity in the solvent. There is, however, no necessity to doubt the existence of a genuinely uncatalysed reaction. In carbon tetrachloride solution, a unimolecular constant of this magnitude would be quite a reasonable one to expect for a reaction having a critical increment of some 26,500 calories. The results themselves are in fact more consistent with the view that the slow reaction in  $\text{CCl}_4$  is uncatalysed, for, as will be shown presently, Lowry and Traill have established that most organic catalysts influence the velocity of this reaction to about the same extent. Taking an average of many values of the catalytic coefficient, it can be shown that a unimolecular constant equal to  $6.66 \times 10^{-6}$  seconds $^{-1}$  at 25° C. in this solvent would necessitate the presence of organic impurity to an extent corresponding to more than 0·001 gram molecule per litre. This is unlikely.

Turning to the influence of catalysts on the velocity of mutarotation, pyridine, alcohol, and *p*-cresol exert very similar effects. The unimolecular constant is found to be linearly related to the concentration of pyridine, but with the other catalysts the same relation only holds in very dilute solutions. Consequently, the catalytic coefficients

† *Proc. Roy. Soc., A*, 132, 398, (1931).

have in these cases been obtained by a slight extrapolation (Table 2, which is taken from Lowry and Traill's paper). As the authors point out, the most interesting feature of this table is the uniformity of the

Table 2

Catalytic coefficients (litres/gram molecule-minute)				
(a) Mutarotation of glucose in water at 20°	(b) Mutarotation of beryllium benzoylcamphor			
[OH <sup>-</sup> ] = 8,000	Pyridine in CCl <sub>4</sub> at 20°	.	.	0.132
[OH <sub>2</sub> ] = 0.00026	Pyridine in CCl <sub>4</sub> at 25°	.	.	0.227
[OH <sub>3</sub> <sup>+</sup> ] = 0.36	Pyridine in CCl <sub>4</sub> at 30°	.	.	0.385
[HCl] = about 0.5	Pyridine in CHCl <sub>3</sub> at 25°	.	.	0.100
[HAc] = 0.0065	Alcohol in CCl <sub>4</sub> at 20°	.	.	0.231†
[Ac <sup>-</sup> ] = 0.069	Alcohol in CCl <sub>4</sub> at 25°	.	.	0.370†
[NH <sub>4</sub> <sup>+</sup> ] = 0.0012	Alcohol in CCl <sub>4</sub> at 30°	.	.	0.658†
	Alcohol in CHCl <sub>3</sub> at 25°	.	.	0.204†
	p-Cresol in CCl <sub>4</sub> at 25°	.	.	0.318†
	p-Cresol in CHCl <sub>3</sub> at 25°	.	.	0.103†
	Acetone in CCl <sub>4</sub> at 25°	.	.	0.015†
	CCl <sub>4</sub> and CHCl <sub>3</sub> at 25°	.	.	{ Negligible in comparison

† Extrapolated to infinite dilution.

catalytic efficiency of pyridine, cresol, and ethyl alcohol, representing a weak base, a weak acid, and a simple organic molecule. This is in striking contrast with the highly specific action of acids and bases upon the mutarotation of glucose in water.

An analysis of these results in terms of the kinetic theory has been given by Traill,† who finds that the equation of Trautz gives values of the catalytic coefficients which are equal to the experimental values to within a factor of about 2.7. A somewhat closer agreement results from independent and slightly different calculations.‡ The results refer to CCl<sub>4</sub> and are given in Table 3. The calculated values of the energy of activation are obtained from the equation

$$\frac{\text{number of molecules reacting}}{\text{total number of collisions}} = e^{-E/RT}. \quad \text{I (35)}$$

Table 3

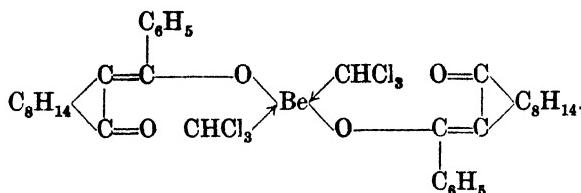
Catalyst	E <sub>observed</sub>	E <sub>calculated</sub>
Pyridine	18,850	18,840
Alcohol	18,410	18,690

† Phil. Mag., 13, 225, (1932).

‡ Moelwyn-Hughes, Nature, 129, 316, (1932).

The disparity in the results of the two calculations, although small, is worth examining, since the choice of reactants, solvent, and catalysts made by Lowry and Traill offer an unusually favourable test of the applicability of the gas-collision formula to calculate the frequency of encounters in dilute solution. For catalysis by alcohol a critical increment of 18,500 calories may be accepted† in preference to the value of 20,200 calories previously published. The other sources of the discrepancy may be traced to the use of a form of the collision equation which gives values that are 10 per cent. higher than those given by equation (21) of Chapter I, and finally to the small correction of  $\frac{1}{2}RT$ . When all these factors are taken into account, the results of Lowry and Traill give an agreement with theory which is as absolute as the uncertainty in estimating the molecular diameters will allow.

Direct experimental proof that complexes between solute and solvent play a definite part in determining the rate of reaction is hard to find, although the necessity for postulating such behaviour frequently arises. An interesting example is afforded by the mutarotation of beryllium benzoylcamphor. Dissolved in carbon tetrachloride or in cyclohexane, the  $\alpha$  and  $\beta$  forms have almost the same stability, so that at equilibrium they are present in equal amounts ( $K = c_\alpha/c_\beta = k_\beta/k_\alpha = 1$ ). In chloroform solution, the ratio becomes 2:3 approximately, indicating, as the authors point out, that this solvent is not only able to combine with the  $\alpha$  and  $\beta$  forms of beryllium benzoylcamphor, but by selective combination with the  $\beta$  form to favour the formation of this variety at the expense of the less soluble  $\alpha$  isomeride. The intermediate compound has been isolated by Burgess and Lowry‡ as a crystalline solvate with two molecules of chloroform; from the value of its optical rotation, the following symmetrical structure has been ascribed to it:



Since the racemization of an optically active compound usually proceeds through the formation of an intermediate compound of higher

† Dr. R. C. Traill, private communication.

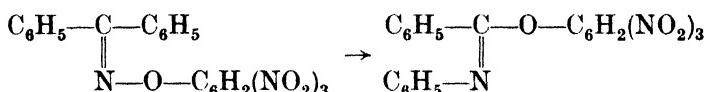
‡ *Trans. Chem. Soc.*, 125, 2081, (1924).

symmetry, the complex thus formulated provides an ideal mechanism for the reaction. From a knowledge of all the specific rotations involved, Lowry and Traill have shown that 46 per cent. of the  $\alpha$  form and 64 per cent. of the  $\beta$  form are combined with the solvent. Experiments prove that these figures account quantitatively for the lessened catalytic activity of pyridine in chloroform, as compared with solutions in carbon tetrachloride, where the whole of the solute is apparently free to interact with the catalyst instead of being bound in part to the solvent. These investigations have accordingly given us a description—possibly as clear and precise as it is possible to expect—of the definite part played by a well-defined intermediate compound in the mechanism of chemical change in solution.

#### *Catalysis of the Beckmann Transformation in Carbon Tetrachloride Solution*

A. W. Chapman's investigation of the kinetics of the Beckmann rearrangement of numerous ketoximes in inert solvents and under the influence of various catalysts takes the subject a whole stage forward by providing the first demonstration of the direct field effect in catalysis.

In carbon tetrachloride solution, the picryl ether of benzophenone oxime undergoes the Beckmann rearrangement



unimolecularly, but the velocity is found to be linearly related to the concentration of catalyst. This Chapman interprets as evidence that, in addition to the unimolecular change proper there is a concomitant change due to catalysis by the oxime itself.<sup>†</sup> Some of the results obtained are reproduced in Table 4. The apparent energy of activa-

*Table 4*

*Unimolecular Velocity Constants and Catalytic Coefficients for the Beckmann Transformation in Carbon Tetrachloride Solution*

$t^{\circ}\text{ C.}$	$k_1 \times 10^6$	$k_2 \times 10^6$
80.5	4.40	67
85.9	7.90	—
92.8	16.8	190
100.0	34.1	392

<sup>†</sup> *Trans. Chem. Soc.*, 1550, (1934).

tion for the unimolecular reaction, corrected for viscosity, is 30,250 calories, and its rate is such as to indicate that a small number of internal degrees of freedom is necessary to sustain the activation. The energy of activation for the catalytic process is 22,620 calories, and the rate is, within a factor of 2, equal to that predicted by the

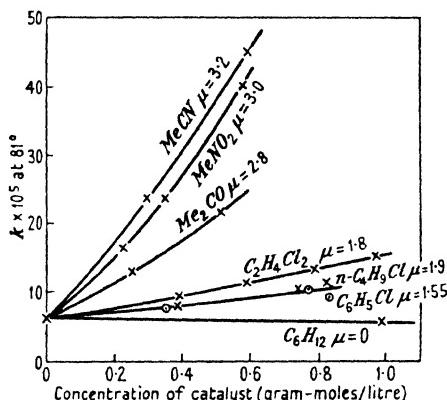


FIG. 1. The catalysis of the Beckmann change by a variety of solutes.†

simple collision theory. Non-polar solutes, such as hexane, have no influence on the rate of transformation; other solutes affect it with an efficiency which increases as the dipole moment (Fig. 1). The slight curvature of some of the lines, and the apparently inhibitive effect of hexane are probably to be attributed to the influence of dilution. The relation between the dipole moments of the catalysts and the energies of activation of the catalytic transformation is shown in Table 5. Within the limits of error, the catalysts affect the reaction by lowering the energy of activation, and are otherwise equally efficient. The figure in brackets is but a rough kinetic estimate of the

*Table 5*  
*Molecular Statistics of the Catalysed Beckmann Change in Carbon Tetrachloride*

Catalyst	$\mu \times 10^{18}$ e.s.u.	$E_a$ (cals./gm. mole)	P
The reactant	(5.4)	22,620	0.43
CH <sub>3</sub> NO <sub>2</sub>	3.0	23,800	0.53
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1.8	24,400	0.26

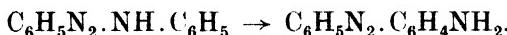
† After A. W. Chapman, *ibid.*, 1550, (1934).

dipole moment of the oxime, consistent with the evident experimental value of 50 calories per gram mole per debye for  $dE/d\mu$ . It is a useful figure because it enables us to ascribe a value of about 10, in the usual units, for  $dE/d(\mu_A \mu_C)$ . Comparison with the figures evaluated on p. 224 shows that the influence of the dipole on the energy of activation is of a lower order of magnitude in reactions catalysed by polar molecules than in those wherein the polar molecules take part, as could have been expected.

It therefore appears that the Beckmann change is facilitated by the presence of even faint electrostatic fields. We must not, however, conclude that any solute molecule possessing a dipole moment will act as a positive catalyst. Chapman has shown that even non-polar molecules may act as catalysts provided the two (internally compensating) dipoles which they contain are sufficiently far apart not to cancel out each other's external fields. Thus, *trans*-dichlorethylene has no catalytic effect, but *p*-dichlorbenzene and *trans*-1:4-dibromcyclohexane are catalytically efficient, the latter being almost as good as ethylene dichloride.

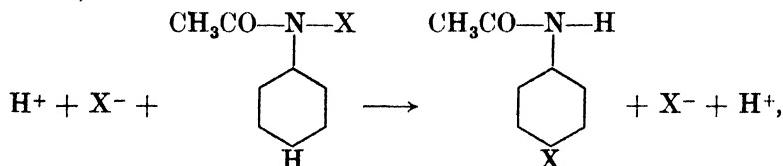
#### *Other Catalytic Reactions in Non-Aqueous Solvents*

A third example of a catalysed reaction in a non-aqueous solvent is the conversion of diazoaminobenzene into *p*-aminoazobenzene in aniline solution, under the catalytic influence of aniline hydrochloride.† The unimolecular constant is linearly related to the concentration of catalyst,  $E_2$  being  $24,020 \pm 1,300$  calories.



The calculated critical increment is 22,000 calories by equation I (35).

We may next consider the rearrangement of the N-halogenoacetanilides,



which has been extensively investigated. In aqueous solution, the rate is proportional to the product of the concentrations of the

† Goldschmidt and Reinders, *Berichte*, **29**, 1369, (1896).

reactant, the halide ion, and the hydrogen ion, † and the great increase in velocity caused by the replacement of chlorine by bromine is fully accounted for by the decrease of 6,800 calories in the energy of activation.‡ The absolute rate is faster than we would expect for a termolecular reaction with the observed energy of activation, but not inconsistent with anticipation for a bimolecular reaction between an elementary ion and a charged complex bearing a charge of opposite sign (Chapter IV). At least, a radius of  $(3.4 \pm 0.4) \times 10^{-8}$  cm. has been shown to cope with most of the facts.§ With the bromine compound in non-aqueous solvents the facts are not so readily understood. Bell|| finds the catalytic process to be, on the collisional basis, a highly inefficient one (Table 6). The catalytic coefficients, in monochlorobenzene solution, are proportional to the dissociation constants of the catalyst, in aqueous solution, raised to the power of 0.3. Some remarks are made later on an empirical relation previously established between catalytic and ionization constants which both refer to the same medium.

*Table 6*  
*Apparent Energies of Activation for the Catalytic Conversion of*  
*N-Bromacetanilide in Chlorobenzene Solution*

Catalyst	$E_A$ (kilocal./gm. mole)	P
$\text{CH}_3(\text{OC}_6\text{H}_5)\text{COOH}$	15.0	$2.8 \times 10^{-5}$
$\text{CH}_3\text{Cl.COOH}$	14.6	$1.4 \times 10^{-5}$
$\text{CH}(\text{C}_6\text{H}_5):\text{CH.COOH}$	13.9	$8.9 \times 10^{-6}$
$\text{CHCl}_2\text{COOH}$	13.8	$1.1 \times 10^{-6}$
$\text{CCl}_3\text{COOH}$	11.8	$8.9 \times 10^{-7}$

Catalysis in liquid ammonia has been extensively investigated, though up to the present at one temperature only.†† The acid-catalysed condensation of  $\omega$ -hydroxy-undecanoic acid in various non-aqueous solvents‡‡ and the acid-catalysed halogenation of unsaturated aldehydes§§ in acetic acid solution both exhibit interesting kinetic features.

† Orton, *Proc. Roy. Soc., A*, **71**, 156, (1902); Rivett, *Z. physikal. Chem., A*, **82**, 201, (1913); Soper and Pryde, *Trans. Chem. Soc.*, 2761, (1927); Belton, *ibid.*, **116**, (1930).

‡ I. Jones and Soper, *Proc. Roy. Soc., A*, **144**, 643, (1934); Olson and Hornel, *J. Organic Chem.*, **3**, 76, (1938).

§ *Proc. Roy. Soc., A*, **155**, 308, (1936). || *Ibid.*, **143**, 377, (1934).

†† Schattenstein, *Z. physikal. Chem., A*, **171**, 286, (1934); *Acta Physicochim. U.S.S.R.*, **6**, 841, (1936).

‡‡ M. M. Davies, *Trans. Faraday Soc.*, **34**, 410, (1938).

§§ La Mare and P. W. Robertson, *Trans. Chem. Soc.*, **888**, (1945).

*The Catalytic Mutarotation of  $\alpha$ -Glucose in Aqueous Solution*

We shall first examine unimolecular constants measured in aqueous solution containing varying concentrations of hydrochloric acid and potassium chloride at constant ionic strength. The unimolecular velocity constant,  $k$ , is the sum of two terms, namely,

$$k = k_0 + k_H c_H, \quad (4)$$

where  $k_0$  is the velocity coefficient of the uncatalysed reaction in the pure solvent,  $k_H$  is the catalytic coefficient, and  $c_H$  is the concentration of hydrogen ions. Both  $k_0$  and  $k_H$  may be obtained by the method of least squares; the experimental values of  $k$  and those reproduced by means of these constants are shown in Table 7.† In Table 8, the values of  $k_0$  thus obtained are compared with those

Table 7

*Unimolecular Velocity Constant for the Mutarotation of  $\alpha$ -d-Glucose in Aqueous Hydrochloric Acid Solution*

$T$ (°K.)	$c_A \times 10$	$c_H \times 10^3$	$k \times 10^4$	
			Observed	Calculated
282.98 ± 0.02	3.11	20.11	1.309	1.305
282.97 ± 0.01	2.99	40.22	1.718	1.723
282.99 ± 0.01	3.30	50.28	1.934	1.932
293.21 ± 0.02	3.91	20.05	3.841	3.817
293.11 ± 0.01	2.68	40.25	5.090	5.185
293.11 ± 0.01	3.16	60.20	6.616	6.536
293.11 ± 0.01	3.55	80.26	7.854	7.895
303.16 ± 0.01	2.50	7.90	7.905	7.95
303.14 ± 0.01	3.31	20.03	10.36	10.31
303.14 ± 0.02	3.75	40.06	14.32	14.22
303.14 ± 0.02	3.78	50.07	16.10	16.17
313.38 ± 0.02	2.98	1.968	16.73	16.68
313.38 ± 0.01	3.35	3.936	17.72	17.76
313.30 ± 0.01	3.32	7.86	19.81	19.93
313.38 ± 0.01	3.15	9.84	21.30	21.02

determined directly in pure water,‡ and the values of  $k_H$  are compared with those obtained from the equation of Arrhenius, with  $E_A = 18,980$  calories. The individual values of  $E_A$  are 19,190, 18,610, and 19,190, indicating a minimum in the neighbourhood of 25° C.,

† P. Johnson and Moelwyn-Hughes, *Trans. Faraday Soc.*, **37**, 289, (1941).

‡ Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc., A*, **176**, 352, (1940).

much as in the ionization of water.<sup>†</sup> An analysis of these results in conjunction with, and giving equal weight to, those of Hudson and

Table 8

$T$ ( $^{\circ}$ K.)	$k_0 \times 10^8$		$k_H \times 10^8$	
	Analytical extrapolation from catalytic experiments	Direct observation from non-catalytic experiments	Observed	Calculated
282.98 $\pm$ 0.02	8.87	8.63	2.08	2.08
293.11 $\pm$ 0.01	24.6	24.7	6.77	6.70
303.14 $\pm$ 0.02	64.1	64.3	19.5	19.7
313.38 $\pm$ 0.01	156	159	55.2	55.1

Dale<sup>‡</sup>, Kilpatrick and Kilpatrick,<sup>§</sup> and Moelwyn-Hughes<sup>||</sup> leads to the equation

$$\log_{10} k_H = 11.657 - 18560/2.303RT.$$

The energy is regarded as accurate to within  $\pm 180$  calories (Table 9).

Table 9

Catalytic Coefficients for the Hydrogen-ion Catalysed Mutarotation of Glucose

$T$ ( $^{\circ}$ K.)	$k_H \times 10^8$		Investigator
	Observed	Calculated	
273.10	0.62	0.64	K. and K.
282.10	2.02	2.08	M.-H.
282.98	2.08	2.12	J. and M.-H.
287.90	3.83	3.69	M.-H.
293.10	7.02	6.72	K. and K.
293.11	6.77	6.72	J. and M.-H.
293.38	6.76	6.87	M.-H.
298.10	10.0	11.1	H. and D.
298.10	12.8	11.1	K. and K.
298.30	11.4	11.4	M.-H.
303.10	17.3	18.9	H. and D.
303.14	19.5	19.0	J. and M.-H.
303.34	19.1	19.4	M.-H.
313.38	55.2	55.1	J. and M.-H.

Both  $k_0$  and  $k_H$  are composite velocity coefficients. In order to convert the observed catalytic coefficient to the essentially bimolecular

<sup>†</sup> Harned and Owen, *Chem. Rev.*, **25**, 31, (1939).

<sup>‡</sup> *J. Amer. Chem. Soc.*, **39**, 320, (1917).

<sup>§</sup> *Ibid.*, **53**, 3698, (1931).

<sup>||</sup> *Z. physikal. Chem.*, **B**, **26**, 272, (1934).

constant governing the interaction of  $\alpha$ -glucose and hydrogen ion, we have, from equation II (7), the relation

$$k_2 = k_H \left( \frac{K}{K+1} \right), \quad (5)$$

where  $K$  is the equilibrium constant. It follows that

$$k_2 = 1.656 \times 10^{11} \times e^{-18850/RT}.$$

If we assume that the catalytic mutarotation of glucose by hydrogen ion in water is a simple bimolecular change, governed by those collisions where the energy in a specified direction exceeds a critical value,  $E$ , then

$$k_2 = Z_0 \left( 1 + \frac{E}{RT} \right) e^{-E/RT}. \quad I (60)$$

Taking  $Z_0$ , the standard collision frequency, to be proportional to  $T^{\frac{1}{2}}$ , it follows that  $E$  is 18,850 calories at 293.25°. Consequently,  $Z_0$  is  $8.19 \times 10^9$  litres per gram mole-second, or  $1.35 \times 10^{-11}$  c.c. per mole-second. The latter quantity should be comparable with the theoretical standard collision frequency

$$Z_0 = S \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}}, \quad I (18)$$

where  $S$  is the target area on the heavy molecule (here glucose) and  $m$  is the mass of the light molecule (here the hydrogen ion). Doubt exists as to whether we should treat the hydrogen ion in water as a permanently solvated structure, with, say, six molecules of water attached to it, or as an elementary ion. On the first supposition  $S$  becomes  $22.63 \times 10^{-16}$  cm.<sup>2</sup>; on the latter  $2.17 \times 10^{-16}$  cm.<sup>2</sup>. Both are reasonable target areas, and we may therefore say that the mutarotation of glucose, under the catalytic action of hydrogen ions, proceeds at the rate expected if all collisions of sufficient violence between the substrate and catalyst lead to optical inversion. This conclusion† holds, as we shall see, for many other cases of hydrogen ion catalysis.

It holds also for the catalysis of the same reaction under the influence of other ions and molecules, for which the energies of activation listed in Table 10 have been found. The most efficient catalyst for this reaction is the hydroxyl ion, for which Lowry (Table 2) obtained a catalytic coefficient of 133 litres per gram mole-second at 20° C., leading us to expect, on the simple collisional

† *Phil. Mag.*, **14**, 112, (1932).

Table 10

Reference	Catalyst	$E_{\text{p}}$ (kilocalories)
(1)	$\text{C}_6\text{H}_5\text{N}$	18·0
(1)	$\text{CH}_3\text{COO}^-$	19·1
(2)	$\text{CH}_3\text{COO}^-$	18·2
(2)	$\text{C}_6\text{H}_5\text{O}^-$	18·5
(2)	$\text{H}_2\text{PO}_4^-$	17·8
(2)	$\text{CH}_3\text{Cl.COOC}^-$	18·4
(3)	$\text{D}_3\text{O}^+$	19·3

(1) Kilpatrick and Kilpatrick, *J. Amer. Chem. Soc.*, **53**, 3698, (1931).

(2) G. F. Smith and M. C. Smith, *Trans. Chem. Soc.*, 1413, (1937).

(3) Moelwyn-Hughes, Klar, and Bonhoeffer, *Z. physikal. Chem.*, **A**, **169**, 113, (1934); Moelwyn-Hughes, *ibid.*, **B**, **26**, 272, (1934).

basis, an energy of activation of  $12\cdot5 \pm 1\cdot3$  kilocalories. The experimental value is difficult to arrive at, though the sum

$$E_{\text{OH}^-} + \Delta H_W - \Delta H_G$$

is readily determined. Here  $\Delta H$  is the increase in heat content attending ionization, and the subscripts refer, respectively, to the water and glucose molecules. From measurements in the temperature range 0–15° C., G. F. Smith† obtains 22·0 for this sum, and concludes that  $E_{\text{OH}^-}$  is 17·7. While the value of  $\Delta H_W$  at 5° C. is known with accuracy to be 14·34, there is much doubt concerning the value of  $\Delta H_G$  adopted by Smith, which, like that afforded by Table VI (19), is probably too high. From conductivity measurements at 0° and 10° C.,  $\Delta H_G$  appears to be 4·4.‡ If we accept this figure,  $E_{\text{OH}^-}$  becomes 12·1, and  $P$  is unity, which is easier to understand than the highly anomalous value of  $10^4$  which results on Smith's supposition. More accurate data, however, are required to decide the point.

Paesu§ has contended that 2-methylglucose mutarotates bimolecularly, but we agree with Riiber and Sørensen, in their standard work on mutarotation,|| that the change is in all probability a unimolecular one.

The enolization of ketones is kinetically so similar to the mutarotation of sugars that we need only add to the discussion given in

† *Trans. Chem. Soc.*, 1824, (1937).

‡ Scudder, *Electrical Conductivities and Ionization Constants of Organic Compounds*, p. 167, Constable, London, (1914).

§ *Berichte*, **58**, 1455, (1925).

|| *Zur Kenntnis der Anomeren Zucker*, *Det. Kgl. Norske Videnskabers Selskabs Skrifter*, 1938, Nr. 1, Trondheim, (1938).

Chapter V the observation that  $P$  is approximately unity for these reactions also.

### *The Catalytic Decomposition of Diazoacetic Ester*

The rate at which nitrogen is evolved from certain aqueous acidic solutions of diazoacetic ester obeys the unimolecular law

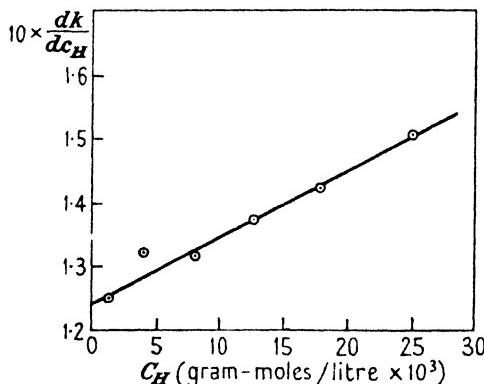
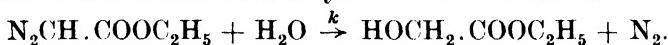


FIG. 2. Hydrogen-ion catalysis of the decomposition of diazoacetic ester.

The unimolecular coefficient,  $k$ , has been shown by Fraenkel† to be linearly related to the concentration,  $c_H$ , of hydrogen ion;

$$k = k_H c_H. \quad (6)$$

His classical researches, however, leave certain points in obscurity. In the first place, a number of strong acids, including HCl, attack the ester molecule effecting substitution, according to the scheme



On account of a partial removal of catalyst, the velocity of elimination of nitrogen falls off at a greater rate than that given by the unimolecular law. In the second place, strong acids which do not appreciably attack the ester according to the substitution mechanism and which consequently give good unimolecular constants, yield catalytic coefficients which vary somewhat with the acid concentration. At 283.16° K., for example, using nitric acid, the unimolecular velocity constant is given by the empirical relation‡

$$k = a + bc_H + dc_H^2, \quad (7)$$

† *Z. physikal. Chem.*, A, 60, 207, (1907).

‡ Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, 37, 1, (1941).

where  $c_H$  is the concentration of hydrogen ion, in gram moles/litre, and  $k$  is the unimolecular velocity coefficient, in reciprocal seconds. The specific constants  $b$  and  $d$  under these conditions have the values 0.124 and 0.525 (Fig. 2).

The conditions of temperature and acid necessary for uncomplicated catalysis must therefore be carefully selected. They are found to correspond to dilute solutions of nitric acid above 10° C., in which region there is no detectable substitution, and the coefficient  $d$  is zero. Some values of the unimolecular velocity coefficients are given in Table 11, from which the catalytic coefficient,  $k_H$ , has been determined by the method of least squares. An analysis of the dependence of  $\ln k_H$  on temperature, shows that either of the equations

$$\ln k_H = 44.6801 - 4.615 \ln T - 18890/RT$$

and

$$\ln k_H = 29.0968 - 17500/RT$$

satisfactorily reproduces the facts. If anything, the latter equation is arithmetically slightly superior, though physically less acceptable. In order to account for the rate of this reaction we find it necessary to postulate the sharing of the activation energy among a small number of degrees of freedom, the first estimate of which† was 4.

In order to explain the specificity of the role of the anion, it appears necessary to conclude that, when the hydrogen ion has replaced the N<sub>2</sub> group, the chloride ion can efficiently compete with the hydroxyl ion for the vacant place, but that the nitrate ion is not so successful.

The value of  $E_A$  given by Fraenkel is 17,560 calories, though his results make possible a value as low as 17,480.‡

### *The Catalytic Decomposition of Nitramide*

Nitramide, which decomposes unimolecularly in aqueous solution,



is sensitive to various solutes, some of which increase and some of which decrease the rate.§ The coefficient,  $k_c$ , in the equation

$$k = k_0 + k_c c \quad (2)$$

† *Phil. Mag.*, **14**, 112, (1932).

‡ Bredig and Fraenkel, *Z. Elektrochem.*, **11**, 515, (1905).

§ Brönsted, *Rec. trav. chim. Pays-bas*, **42**, 718, (1923); Brönsted, Nicholson, and Delbanco, *Z. physikal. Chem.*, **A**, **169**, 379, (1934).

Table 11

*Unimolecular Velocity Coefficients, in Reciprocal Seconds, for the Decomposition of Diazoacetic Ester in Aqueous Nitric Acid Solution*

Temperature (°K.)	$c_H \times 10^4$	$c_E \times 10^2$	$k \times 10^4$	
			Observed	Calculated
273.22 ± 0.02	53.67	3.76	2.190	2.194
273.23 ± 0.01	71.61	1.56	2.982	2.969
273.29 ± 0.03	107.4	3.09	4.509	4.519
273.31 ± 0.02	214.8	1.90	9.168	9.166
273.29 ± 0.03	286.5	1.31	12.78	12.27
278.11 ± 0.04	17.90	3.94	1.296	1.311
278.11 ± 0.04	35.80	3.24	2.641	2.71
278.11 ± 0.04	107.4	1.67	8.45	8.31
278.11 ± 0.04	214.9	0.95	16.65	16.71
283.16 ± 0.03	26.85	3.22	3.351	3.359
283.16 ± 0.03	53.69	2.72	6.907	6.902
283.17 ± 0.03	107.4	2.24	13.98	13.99
283.16 ± 0.05	143.2	0.92	18.90	18.71
283.16 ± 0.03	214.7	1.60, 2.49	29.08	28.15
283.16 ± 0.03	286.5	1.38	39.88	37.64
288.00 ± 0.01	13.46	3.62	2.619	2.675
288.00 ± 0.01	26.83	3.62	5.837	5.785
288.00 ± 0.01	53.65	2.96	11.99	12.00
288.00 ± 0.02	107.3	1.28	24.41	24.43
293.39 ± 0.01	13.45	4.19	4.796	4.92
293.39 ± 0.01	26.80	1.50, 3.26	10.24	10.11
293.39 ± 0.01	53.60	3.10	20.57	20.54
293.39 ± 0.01	107.2	1.90	41.37	41.41
298.11 ± 0.01	13.40	3.84, 2.80	8.03	8.19
298.11 ± 0.01	26.78	1.89	16.9	16.87
298.11 ± 0.01	35.70	1.93	22.7	22.66
298.11 ± 0.01	53.56	1.16	34.4	34.25
298.11 ± 0.01	71.39	0.671, 2.98, 3.36	44.4	45.82
298.11 ± 0.01	107.1	1.49, 1.19	68.9	68.99
303.13 ± 0.03	5.350	3.48	3.625	3.784
303.13 ± 0.04	13.42	2.78	12.43	12.32
303.13 ± 0.04	26.75	2.23	26.51	26.42
303.13 ± 0.04	53.50	1.76	54.64	54.74
308.33 ± 0.03	2.671	4.94	2.293	2.33
308.33 ± 0.03	5.342	4.36	6.705	6.77
308.33 ± 0.03	7.118	2.17	9.835	9.72
308.33 ± 0.03	26.69	2.04	42.23	42.25
313.20 ± 0.04	2.665	3.02	3.785	3.323
313.20 ± 0.04	5.325	2.72	10.23	10.36
313.18 ± 0.05	13.36	1.92	30.74	31.63
313.20 ± 0.04	17.76	1.27	43.76	43.28
313.20 ± 0.04	26.65	1.91	66.92	66.80

may thus have positive or negative values, as is illustrated in Fig. 3.  $k_0$  at  $24.84^\circ\text{C}$ . is  $4.74 \times 10^{-5} \text{ sec.}^{-1}$ ;  $k_H$  is  $1.26 \times 10^{-5} \text{ litres/gm. mole-second}$ , and  $k_{Na}$  is  $-0.94 \times 10^{-5}$  in the same units. The opposite effects of these two ions is, perhaps, the most noteworthy feature of

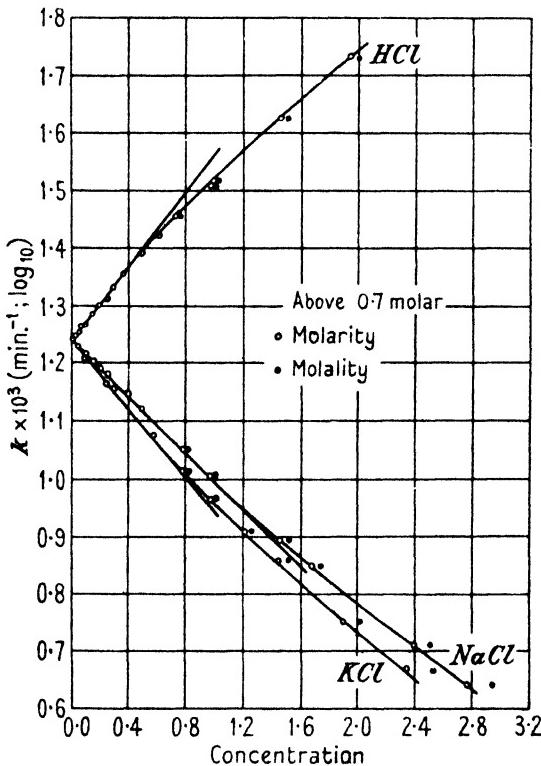


FIG. 3. Unimolecular velocity coefficients ( $\log_{10}$ : minutes $^{-1}$ ) for the decomposition of nitramide in water at  $24.84^\circ\text{C}$ .†

the reaction.‡ Thus the presence of 2 moles of hydrochloric acid per litre of solution increases the rate by 40 per cent., while the same concentration of potassium or sodium chloride decreases the rate to the same extent. In highly concentrated and equimolar solutions of salt and acid, the rate would presumably be the same as in pure water. The electrolyte effect, in the light of equation V (12), indicates that the ion responsible for catalysis in neutral solution approaches that end of the highly polar nitramide molecule which is of opposite polarity to itself.

† After La Mer and Marlies, *J. Amer. Chem. Soc.*, **57**, 1812, (1935).

‡ Cf. von Halban, Kortüm, and Seiler, *Z. physikal. Chem.*, **A**, **173**, 449, (1935).

Let us consider the velocity,  $k_0$ , of the water reaction. From its magnitude we can estimate the energy of activation, using the formula

$$k_0 = \frac{3\pi\eta\sigma}{2m} e^{-E/RT} \quad \text{IX (5)}$$

and giving  $\sigma$  a rough value of  $2.5 \text{ \AA}$ .  $E$  then becomes 21,720, and, since  $B$  at this temperature is 4,020 calories, we expect  $E_A$  to be about 17,700 calories. Only an approximate experimental value is available; Marlies and La Mer, combining their own results at one temperature with those of Brönsted and his collaborators at another temperature not fully  $10^\circ$  away, obtain  $E_A = 18,900$ .

When the molar concentration of acid is about 0.5, the velocity passes through a minimum, indicating that the hydroxyl ion also is a catalyst. From Marlies and La Mer's value of  $k_{OH}$ , we obtain the ratio  $k_{OH}/k_H$  to be  $3 \times 10^9$ , which is consistent with

$$E_H - E_{OH} = 13,000 \text{ calories},$$

a difference which, as we shall see, is higher than is usually found. A still greater difference is found in the following way. Suppose the rate in water and in dilute acidic solution can be represented by the equation

$$k = k_0 + k_H c_H + k_{OH} c_{OH}, \quad (8)$$

then, as Wijs† first proved in his well-known kinetic determination of the ionic product of water, the minimum rates and concentrations are related as follows:‡

$$\left(\frac{k_{OH}}{k_H}\right)_{\min} = \left(\frac{c_H}{c_{OH}}\right)_{\min}. \quad (9)$$

The ratio  $k_{OH}/k_H$  now becomes  $9.5 \times 10^{13}$ , and  $E_H - E_{OH}$  is 19,070 calories. If this analysis is correct, no energy of activation is required by the hydroxyl ion catalysis, each encounter between  $\text{OH}^-$  and nitramide being sufficient to ensure decomposition. Other mechanisms have been advanced, for example, by Pedersen.§ It is doubtful whether a final answer can be given before the structure of nitramide|| is elucidated.

† *Z. physikal. Chem.*, **12**, 514, (1893).

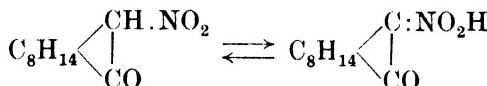
‡ Let  $c_{OH} = K_W/c_H$ . Then  $k = k_0 + k_H c_H + k_{OH} K_W/c_H$ . Equate  $dk/dc_H$  to zero for the minimum.

§ *J. phys. Chem.*, **38**, 581, (1934).

|| Cf. Hantzsch, *Berichte*, **66 B**, 1566, (1933).

*Lowry's Theory of Prototropic and Hydrolytic Changes*

The mutarotation of nitrocamphor can be attributed to the partial conversion of the nitrocompound into an isomer.† The change is seen to involve the migration of a hydrogen atom, and a rearrangement of bonds.



Reducing and oxidizing agents, however, which can furnish or remove hydrogen atoms, have no influence on the change, hence the real migratory unit must be the proton. It is with such changes that the theory of Lowry has to deal. To the mutarotation of sugars, the enolization of ketones, and other chemical transformations which can be represented by the migration of a proton, Lowry has given the name of prototropy.‡ The study of these reactions has led to the development of an electrolytic theory of catalysis which has a bearing on chemical changes other than those for the interpretation of which it was invented. The presentation of the theory has been given in detail by its author.§

Nitrocamphor undergoes mutarotation more slowly in hydrocarbon solvents than in hydroxylic solvents and esters (cf. Menschutkin's results on the formation of tetraethylammonium iodide). The change is not conditioned, however, by the presence of an oxygen atom in the solvent molecule|| nor by the dissociating power (high dielectric constant) of the solvent. Two discoveries have indicated the true conditions. (1) The mutarotation of several compounds can be suspended entirely in certain pure non-aqueous solvents. Tetramethylglucose does not undergo change in dry pyridine, nor in dry cresol.†† With specially cleaned silica vessels, and solvents stringently purified, tetramethylglucose and tetracetylglucose may be kept unchanged for several hours in chloroform, benzene, methyl acetate, and other solvents.†† (2) Although pure pyridine and pure cresol separately do not catalyse mutarotation, a mixture of the two acts as an even more effective catalyst than water. The results show that the change is

† Lowry, *Trans. Chem. Soc.*, **75**, 213, (1899).

‡ *Idem, ibid.*, **123**, 828, (1923).

§ *Idem, Réunion internationale de chimie physique*, p. 219, (1928).

|| Lowry and Magson, *Trans. Chem. Soc.*, **93**, 119, (1908).

†† Lowry and Faulkner, *ibid.*, **127**, 2884, (1925).

‡‡ Lowry and Owen, *Proc. Roy. Soc., A*, **119**, 505, (1928).

not spontaneous: the condition for its inception is the presence of an amphoteric medium. The facility of prototropic changes in water thus becomes readily intelligible. Since the solvent is amphoteric, it can furnish the substrate molecule with a proton at one position and remove a proton from another position. The intramolecular change is then formulated as a transmission of an electron through the molecule, attended by the passage of a proton through the amphoteric solvent. The process accordingly resembles electrolysis, in which the substrate molecule is the electrolyte. For the general application of this idea, the original papers of Lowry must be consulted. The aspect of the theory which is of immediate importance to us is that prototropic and hydrolytic changes proceed by consecutive stages. When, for example, they are catalysed by acids in aqueous solution, the following steps are involved: (1) the reactant molecule collides with a proton-donor, giving rise to an acid complex; (2) this complex collides with a molecule of water; whereby (3) internal electrolysis of the reactant molecule results, the water acting as a proton-acceptor in the case of prototropy and as a hydroxyl-donor in the case of hydrolysis. Since stage (3) may be regarded as instantaneous, there are left two stages either of which may determine the velocity. The study of the kinetics of hydrolytic reactions in the light of these views is taken up at a later stage.

The crucial experiment upon which the present theory rests is that of mutarotation in pyridine-cresol mixtures. The study of other types of chemical changes in 'synthetic' amphoteric solvents would be of great interest.

It is significant that esterification<sup>†</sup> and the saponification<sup>‡</sup> of esters take place much more rapidly in alcoholic solution than in water, and that the addition of water to organic solvents frequently has a marked inhibitive action.<sup>§</sup>

#### *The Order of Magnitude of the Water Coefficient*

The coefficient,  $k_0$ , usually referred to as the water coefficient, is simply the unimolecular constant attributed to the pure solvent, when, as far as possible, the part played by all ions and other solutes has been eliminated. In so far as pure water contains both hydrogen

<sup>†</sup> Goldschmidt and Udry, *Z. physikal. Chem.*, **60**, 728, (1907).

<sup>‡</sup> Gilby and Waters, *Trans. Chem. Soc.*, 2643, (1932).

<sup>§</sup> Goldschmidt, *Berichte*, **29**, 2208, (1896); Lapworth and Fitzgerald, *Trans. Chem. Soc.*, **93**, 2167, (1908).

and hydroxyl ions,  $k_0$  for this solvent may be something of a kinetical fiction. For suppose that, in pure water, the real catalyst is one of these ions: the rate of reaction is then governed, not so much by the constant concentration of ions in solution but by the rate at which they are produced in the vicinity of the reactant. The chance per second that a solute molecule reacts is then the product of the probability of its being in contact with a water molecule and the probability per second that the water molecule shall dissociate. The first of these amounts to a certainty. The chance per second that a water molecule shall ionize equals the unimolecular rate of dissociation, which, from equations (67) and (68) of Chapter VI, we have roughly estimated as

$$k_1 = \frac{3\pi a\sigma}{2m} e^{-(\Delta H_W + B)/RT}. \quad (10)$$

Here  $a$  and  $B$  are the viscosity constants, and  $\Delta H_W$  is the heat of neutralization of strong acids and bases. Both  $B$  and  $\Delta H_W$  are functions of the temperature. At 25° C., however, taking  $\sigma$  as  $2.685 \times 10^{-8}$  cm., we have  $B = 4,020$  and  $\Delta H_W = 13,480$  calories, so that

$$k_1 = 4.3 \times 10^{10} e^{-17500/RT}. \quad (11)$$

Such conditions appear to suffice to account for the water coefficient in the mutarotation of glucose, the decomposition of nitramide, and certain other simple reactions. Higher values of  $E_A$ , however, denote their inadequacy generally, though in quite complicated reactions  $k_1$  may prove to be a key rate.

#### *The Order of Magnitude of the Hydrogen-ion Catalytic Coefficient*

We confine attention here to the relatively simple case where solute molecules are activated by both catalyst (hydrogen ion) and solvent (water), and are deactivated only by the latter. Let

$n_S$  = number of substrate molecules per c.c.

$n_H$  = , hydrogen ions ,

$n_W$  = , water molecules ,

and  $n_A$  = number of activated molecules produced per second by collisions between substrate molecules and hydrogen ions, and by collisions between substrate molecules and water molecules.

Then rate of activation =  $k_1 n_S n_H + k_2 n_S n_W$ ,

rate of deactivation =  $k_3 n_A n_W$ ,

rate of reaction =  $k_4 n_A$ .

The condition for a stationary concentration of active molecules (equation I (39)) gives us

$$n_A = \frac{k_1 n_S n_H + k_2 n_S n_W}{k_4 + k_3 n_W};$$

whence

$$\text{rate of reaction} = k_4 n_A = \frac{k_1 n_S n_H + k_2 n_S n_W}{1 + \frac{k_3}{k_4} n_W}. \quad (12)$$

With considerable deactivation the unimolecular constant is thus

$$k = \frac{k_4}{k_3} \left( k_2 + \frac{k_1}{n_W} n_H \right) \quad (13)$$

and with negligible deactivation it is

$$k = k_2 n_W + k_1 n_H. \quad (14)$$

(Many elaborations of these formulae will be found in the literature.) Only the latter can be tested. According to equation I (30), the rate of the catalytic process is

$$-\frac{dn_s}{dt} = \frac{3\pi\sigma\eta}{4m_s n_W} n_s n_H e^{-E/RT}. \quad (15)$$

This expression adequately accounts for the rate of hydrolysis of esters, amides, and glycines under the catalytic action of hydrogen ions,<sup>†</sup> for the rate of decomposition of hydrogen peroxide<sup>‡</sup> catalysed by the same ion in various solvents, and for the rates of hydrolysis and alcoholysis of phenyl acetate in mixtures of alcohol and water.<sup>§</sup> More complicated changes require internal activation to maintain a Maxwellian distribution, and the minimum values of  $F$  thus needed are given in Table 12.

The mechanism of esterification<sup>||</sup> is naturally more complicated than that of hydrolysis, and the catalytic coefficient is not so easy to estimate. There is, nevertheless, a steady progress discernible in this difficult field.<sup>††</sup>

From the standpoint of molecular statistics, there is clearly nothing

<sup>†</sup> *Phil. Mag.*, **14**, 112, (1932).

<sup>‡</sup> Hender and R. A. Robinson, *Trans. Faraday Soc.*, **29**, 1300, (1933).

<sup>§</sup> Waters, *Trans. Chem. Soc.*, 1014, (1936).

<sup>||</sup> Goldschmidt, *Z. physikal. Chem.*, **60**, 728, (1907).

<sup>††</sup> Kilpi, *ibid.*, **A**, **141**, 424, (1929); **166**, 285, (1933); Rolfe and Hinshelwood, *Trans. Faraday Soc.*, **30**, 936, (1934); A. T. Williamson and Hinshelwood, *ibid.*, p. 1145; Hinshelwood, *Trans. Chem. Soc.*, 599, (1935); M. M. Davies, *Trans. Faraday Soc.*, **33**, 331, (1937).

to distinguish catalysis by hydroxyl ion from catalysis by hydrogen ion, as the one example included in Table 12 makes clear. Moreover, when equation (15) is applied to the hydrolysis of esters by alkalis (Table V (4)), the ratio of  $k_{\text{calculated}}/k_{\text{observed}}$  becomes 14, which is a more plausible value than that of 25,000 obtained when no allowance is made for the variation of collision frequency with temperature. Saponification, however, is a chemical change involving, and not a catalysis by, hydroxyl ion. We must content ourselves with one example of hydroxyl ion catalysis.

Table 12

Reference	Reaction catalysed by hydrogen ion	$E_A$	$A$	$E$	$t^{\circ}\text{C}$ .	$k = k_i/[\text{catalyst}]$		$F$
						Observed	Calculated	
(1)	Hydrolysis of methyl acetate	16,920	$3.86 \times 10^8$	20,790	30	$2.16 \times 10^{-4}$	$2.55 \times 10^{-4}$	0
(2)	Hydrolysis of ethyl acetate	16,830	$1.66 \times 10^8$	20,840	25	$9.38 \times 10^{-5}$	$1.23 \times 10^{-4}$	0
(3)	Hydrolysis of acetamide	18,780	$9.43 \times 10^8$	22,790	25	$6.60 \times 10^{-4}$	$6.79 \times 10^{-4}$	0
(4)	Conversion of creatine into creatinine	19,690	$4.35 \times 10^8$	22,810	78	$2.18 \times 10^{-4}$	$4.08 \times 10^{-4}$	0
(5)	Hydrolysis of benzoyl glycine	22,100	$1.72 \times 10^8$	25,210	80	$5.05 \times 10^{-4}$	$1.13 \times 10^{-4}$	0
(5)	Hydrolysis of acetyl glycine	22,100	$7.41 \times 10^8$	25,430	60	$2.05 \times 10^{-4}$	$2.77 \times 10^{-4}$	1
(6)	Conversion of $\gamma$ -hydroxyvaleric acid into lactone	16,630	$4.55 \times 10^8$	20,500	30	$4.38 \times 10^{-4}$	$3.38 \times 10^{-4}$	1
(7)	Enolization of acetone	20,580	$3.94 \times 10^{10}$	24,620	24	$2.53 \times 10^{-4}$	$3.63 \times 10^{-4}$	2
(8)	Decomposition of nitrosotriacetonamine (catalysed by $\text{OH}^-$ )	16,040	$4.69 \times 10^8$	19,910	30	$3.04 \times 10^{-4}$	$4.09 \times 10^{-4}$	2
(9)	Decomposition of diazoacetic ester	17,480	$4.64 \times 10^{11}$	21,490	25	$6.42 \times 10^{-1}$	$1.63 \times 10^{-1}$	4
(10)	Hydrolysis of lactose	24,680	$3.21 \times 10^{11}$	28,890	25	$3.24 \times 10^{-7}$	$3.12 \times 10^{-7}$	4
(11)	Hydrolysis of sucrose	25,560	$8.89 \times 10^{14}$	29,570	25	$1.41 \times 10^{-4}$	$9.82 \times 10^{-4}$	10
(12)	Hydrolysis of maltose	30,970	$1.86 \times 10^{11}$	34,300	60	$1.68 \times 10^{-4}$	$2.00 \times 10^{-4}$	9
(12)	Hydrolysis of cellobiose	30,710	$9.78 \times 10^{14}$	34,040	60	$5.89 \times 10^{-4}$	$5.47 \times 10^{-4}$	9

- (1) Lamble and Lewis, *Trans. Chem. Soc.*, **105**, 2330, (1914).
- (2) Taylor, *J. Amer. Chem. Soc.*, **37**, 551, (1915).
- (3) Meehan, *Thesis*, Liverpool, (1923); Euler and Rudberg, *Z. anorg. Chem.*, **127**, 244, (1923); von Peckoff and Meyer, *Z. physikal. Chem.*, **82**, 129, (1913); Crocker, *Trans. Chem. Soc.*, **91**, 573, (1907).
- (4) Edgar and Wakefield, *J. Amer. Chem. Soc.*, **45**, 2242, (1923).
- (5) Escombe and Lewis, *Trans. Faraday Soc.*, **23**, 651, (1927).
- (6) Garrett and Lewis, *J. Amer. Chem. Soc.*, **45**, 1091, (1923); Taylor and Close, *J. Physical Chem.*, **29**, 1085, (1925).
- (7) Rice, Fryling, and Wesolewski, *J. Amer. Chem. Soc.*, **46**, 2405, (1924); Rice and Kilpatrick, *ibid.*, **45**, 1401, (1923); Dawson and Powis, *Trans. Chem. Soc.*, **101**, 1502, (1912); see also Dawson and co-workers in subsequent issues of this journal.
- (8) Clibbens and Francis, *ibid.*, **101**, 101, (1912); Colvin, *Trans. Faraday Soc.*, **22**, 241, (1926).
- (9) Fraenkel, *Z. physikal. Chem.*, **60**, 202, (1907).
- (10) Bleyer and Schmidt, *Biochem. Z.*, **135**, 546, (1923); Moelwyn-Hughes, *Trans. Faraday Soc.*, **24**, 309, (1928).
- (11) Urech, *Berichte*, **17**, 2175, (1884); Spohr, *Z. physikal. Chem.*, **2**, 195, (1888); Arrhenius, *ibid.*, **4**, 226, (1889); Lamble and Lewis, *Trans. Chem. Soc.*, **107**, 233, (1915); Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 81, (1929).
- (12) Moelwyn-Hughes, *ibid.*, **25**, 503, (1929).

### The Catalytic Decomposition of Diacetone-alcohol

The proportionality of the rate of decomposition of diacetone-alcohol to the concentration of hydroxyl ion in aqueous solution,



was established by French,<sup>†</sup> whose unimolecular constants are shown

<sup>†</sup> *J. Amer. Chem. Soc.*, **51**, 3215, (1929); see also Åkerlöf, *ibid.*, **48**, 3046, (1926).

in Table 13. Within a twentyfold range of catalyst concentration the catalytic coefficient is seen to be constant to within  $\pm 1.5$  per cent., though there are indications of a slight positive electrolyte effect.

Table 13

*Catalytic Coefficients for the Decomposition of Diacetone-alcohol at 25° C.*

[NaOH] $\times 10^3$ (gm. moles/litre)	$k \times 10^3$ (min. $^{-1}$ ; $\log_{10}$ )	$k/[NaOH]$
5	1.01	0.202
10	2.03	0.203
20	4.08	0.204
40	8.33	0.208
100	20.80	0.208

Expressed in the customary units, the catalytic coefficient at this temperature is thus  $7.87 \times 10^{-3}$ . Murphy† measured the temperature effect with concentrations of alkalis varying between 0.01 and 0.10 molar. The mean of eight values of  $k_{30}/k_{20}$  is 2.57 and of  $k_{35}/k_{25}$  is 2.67, which gives us, respectively, 17,918 and 18,122 calories as the apparent energy of activation. Within the limits of error we may take  $E_A$  to be  $18,020 \pm 100$  calories at 27.5° C. On combining this with French's catalytic coefficient we obtain

$$k_2 = 1.31 \times 10^{11} \times e^{-18020/RT},$$

from which at a glance we recognize a reaction proceeding with the normal velocity.

La Mer‡ has given a different interpretation of the same set of results, from an analysis of which he deduced that  $E_A$  increased markedly with a rise in temperature ( $dE_A/dT = +211$  calories/gm. mole-degree). In a careful repetition of the experiments,§ a catalytic coefficient exceeding the earlier value by about 8 per cent. is found in a somewhat narrower concentration region, and an increase in  $E_A$  with a rise in temperature has been verified. The increase is not, however, as great as La Mer's first estimate. The point-to-point values of  $E_A$  and  $A$  calculated by La Mer and Miller are reproduced in Table 14, to which have been added the corrected energies  $E = (E_A + B)$ . It will be observed that  $E$  is less variable than  $E_A$ , and, from 5 to 40° C., has an average value of  $20,990 \pm 360$  calories. Inspection of the  $E_A$  figures shows that two of them may differ at

† *J. Amer. Chem. Soc.*, 53, 977, (1931).

‡ *J. Chem. Physics*, 1, 289, (1933).

§ La Mer and (Miss) M. L. Miller, *ibid.*, 57, 2674, (1935).

the same temperature by 210 calories. A further error of 150 calories in  $RT^2(d \ln \eta/dT)_P$  is not an unreasonable one to allow when we consider the effect of the various solutes on the viscosity. Within the limits of error, therefore, we conclude that  $E$  is constant. The presence of methyl alcohol diminishes  $B$  and increases  $E_A$ , so that the introduction of the viscosity correction here, as in other cases, seems to explain at least one of the factors in the solvent effect. In cases such as the present one, however, kinetic work has far outstripped our knowledge of the static properties of the system. As far as one is able to apply equation I (30), there results, as La Mer and Miller observe, a good correlation.

Table 14

*Apparent Energies of Activation ( $E_A$ ) and Corrected Values ( $E = E_A + B$ ) for the Catalytic Decomposition of Diacetone-alcohol by Hydroxyl ion in water  
(' for 15° interval, " for 20°, others for 10°.)*

Mid-point of temp. interval, °C.	A moles litre/min.	$E_A$	$E$
4.89	10.92	15,850	20,630
7.49	11.13'	16,100'	20,760
9.96	11.22"	16,230"	20,780
10.42	11.42	16,500	21,030
12.89	11.46'	16,550'	20,980
14.85	11.52	16,620	20,970
15.43	11.56"	16,680"	21,010
17.39	11.63	16,770'	21,030
19.84	11.75"	16,920"	21,140
19.99	11.69	16,850	21,020
22.44	11.83'	17,040'	21,130
24.91	11.97	17,250	21,260
24.97	11.84"	17,040"	21,080
27.44	11.93	17,180'	21,020
29.96	11.96"	17,220"	21,090
29.98	11.98	17,240	21,110
32.50	12.00'	17,270'	21,080
34.95	11.94	17,190	20,940
35.05	12.02"	17,290"	21,040
37.50	11.98'	17,250'	20,940
39.93	11.78"	16,960"	20,600
40.04	12.05	17,350	20,990
42.47	11.76'	16,930'	20,560
44.99	11.61	16,720	20,288

#### *A Comparison of Catalysis by Hydrogen Ion and Hydroxyl Ion*

It has long been known that hydroxyl ions are more efficient catalysts for many reactions than are hydrogen ions. According to the mechanism of catalysis which was shown in the preceding sections

to be most commonly at work in solutions, we should anticipate a lower critical increment for the basic catalysis. The anticipation is fully justified, as the results in Table 15 indicate. The data, which

Table 15

Reaction	$E_A$		Difference
	Catalysed by hydrogen ion	Catalysed by hydroxyl ion	
Decomposition of nitrosotriacetone-amine	22,100	16,210	5,890
Hydrolysis of methyl acetate	16,920	11,220	5,700
Hydrolysis of ethyl acetate	16,830	11,210	5,620
Conversion of hexamethylpararosaniline hydrochloride from carbinal to quinonoid form†	17,770 18,910 19,460	11,260 12,950 13,750	6,510 5,960 5,710
Hydrolysis of acetamide	19,210	13,320	5,890
Hydrolysis of propionamide	19,490	12,930	6,560
Hydrolysis of butyramide‡	18,890	13,870	5,020

† This reaction is probably not simple, the critical increments falling with rise in temperature. Nevertheless ( $E_H - E_{OH}$ ) remains roughly constant at all temperatures. The reaction was measured by Biddle and Porter (*J. Amer. Chem. Soc.*, **37**, 1571, (1915)).

‡ Crocker (*loc. cit.*) whose results with alkalis are probably liable to considerable error. References to the other sources of information have already been given.

refer to aqueous solutions, point to an approximately fixed value of 5,980 calories for ( $E_H - E_{OH}$ ) in the case of all these reactions. At 25° C., the ratio  $k_{OH}/k_H$  of the catalytic coefficients in the case of the mutarotation of glucose (Table 2) is  $2.22 \times 10^4$  and in the case of the enolization of acetone†  $4.3 \times 10^4$ . Assuming the collision frequency to be the same for basic and acidic catalysis, we have

$$\Delta E = RT \ln(k_{OH}/k_H).$$

For mutarotation ( $E_H - E_{OH}$ ) thus becomes 5,910 calories, and for the acetone-iodine reaction, 6,310 calories. Although the temperature coefficients of these reactions, catalysed by hydroxyl ion, have not been measured experimentally, we can with some confidence predict the values of  $E_{OH}$  to be 13,600 and 14,600 calories respectively.

Without pretending to know why the energy difference is approximately constant, we may use the fact to determine the variation with

† Dawson, *Trans. Chem. Soc.*, **458**, 2449, (1927).

temperature of the pH corresponding to the minimum velocity. From Wijs's relation (9), we have

$$[\text{H}^+]_i = \sqrt{\frac{k_{\text{OH}} K_W}{k_{\text{H}}}}, \quad (16)$$

whence

$$\frac{d(\text{pH})_i}{dT} = \frac{E_{\text{H}} - E_{\text{OH}} - \Delta H_W}{2 \times 2.303 \times RT^2}. \quad (17)$$

$\Delta H_W$  is the heat of ionization of water (13,700 calories), hence the numerator becomes roughly  $-7,800$  calories. This means that the pH corresponding to the minimum velocity has a negative temperature coefficient, which is nearly the same for all hydrolytic reactions. A rise in temperature from 20 to 30°C. reduces  $(\text{pH})_i$  by nearly 0.1.

In aqueous acetone solution, the difference  $E_{\text{H}} - E_{\text{OH}}$  is about 1.3 kilocalories less than in water.<sup>†</sup> Comparable results in the catalytic decomposition of the dithionite ion ( $\text{S}_2\text{O}_6^{2-}$ ) have also been reported.<sup>‡</sup>

#### *A Comparison of Catalytic Hydrolysis and Deuterolysis*

Reactions of deuterium atoms and molecules in the gas phase are usually slower than the corresponding reactions of hydrogen.<sup>§</sup> The difference,  $E_{\text{D}} - E_{\text{H}}$ , when each energy is computed from the equation  $E = RT^2 d \ln k / dT$ , is about 2 kilocalories. Part of the tardiness is undoubtedly due to the heavier mass of the new isotope, but, after allowing for this difference,  $E_{\text{D}} - E_{\text{H}}$  is still about 1 kilocalorie, which can be chiefly accounted for by differences in residual energies.<sup>||</sup>

A similar state of affairs prevails in certain solutions. The uncatalysed mutarotation of glucose in water, for example, is roughly 3 times as fast as the corresponding change in liquid deuterium oxide, and the catalytic efficiency of the deuterated deuterium ion ( $\text{D}_3\text{O}^+$ ) towards the same reaction is only about two-thirds that of the hydrated hydrogen ion ( $\text{H}_3\text{O}^+$ ). As a rule, however, the position in solution is reversed, i.e. the reaction involving D is faster than that involving H. This is true not only for those cases listed in Table 16, which summarizes the information available on the changes in activation energy, but for very numerous reactions which have been measured at single temperatures only and to which detailed reference

<sup>†</sup> Newling and Hinshelwood, *ibid.*, 1357, (1936).

<sup>‡</sup> Goldfinger and von Schweinitz, *Z. physikal. Chem.*, **B**, 22, 117, (1933).

<sup>§</sup> *Ann. Reports Chem. Soc.*, 33, 86, (1937).

<sup>||</sup> Farkas and Farkas, *Light and Heavy Hydrogen*, Cambridge, (1935).

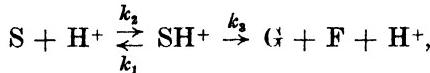
cannot here be given. The contrast between the isotopic effects in mutarotation and hydrolysis is rather remarkable, and has been the subject of much speculation. Moelwyn-Hughes and Bonhoeffer† have suggested that mutarotation and hydrolysis differ in that the rate of the former is governed by the rate of activating collisions between ion and sugar, whereas the rate of the latter is governed by the rate

*Table 16*  
*The Comparative Energetics of Hydrolysis and Deuterolysis*

Reference	Reaction	Catalysts	$k_D/k_H$ at 25° C.	$E_A(H) - E_A(D)$ cal./gm. mole
(1)	Mutarotation of $\alpha$ -d-glucose	$H_2O$ and $D_2O$	0.32	0
(2)	Mutarotation of $\alpha$ -d-glucose	$H_3O^+$ and $D_3O^+$	0.64	-1,250
(3)	Hydrolysis of sucrose	$H_3O^+$ and $D_3O^+$	1.76	1,450
(4)	Hydrolysis of methyl acetate	$H_3O^+$ and $D_3O^+$	1.68	1,200
(5)	Hydrolysis of ethyl orthoformate	$H_3O^+$ and $D_3O^+$	2.50	1,400

- (1) Moelwyn-Hughes, Klar, and Bonhoeffer, *Z. physikal. Chem.*, **A**, **169**, 113, (1934).
- (2) Moelwyn-Hughes, *ibid.*, **B**, **26**, 272, (1934).
- (3) Moelwyn-Hughes and Bonhoeffer, *Naturwiss.*, **11**, 174, (1934); also ref. 2.
- (4) Hornel and J. A. V. Butler, *Trans. Chem. Soc.*, 1361, (1936).
- (5) Brescia and La Mer, *J. Amer. Chem. Soc.*, **62**, 612, (1940).

of decomposition of an ion-sugar complex. According to the familiar scheme



the general expression for the catalytic coefficient,  $k$ , becomes

$$k = \frac{k_2 k_3}{k_1 + k_3}, \quad (18)$$

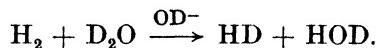
which reduces to  $k_2$  when  $k_3 \gg k_1$ , as in mutarotation, and to  $k_3(k_2/k_1) = k_3/K$  when  $k_1 \gg k_3$ , as in hydrolysis. They consequently attribute the enhanced rate of hydrolysis in deuterium oxide to the greater stability of the complex, as reflected in a lower value of its dissociation constant,  $K$ . Wynne-Jones,‡ arguing that the rate of proton transfer is characteristic of generalized acid catalysis, while the rate of complex dissociation may be characteristic of specific

† *Z. Elektrochem.*, **40**, 469, (1934).

‡ *Chem. Rev.*, **17**, 115, (1935).

hydrogen ion catalysis, has suggested the diagnostic use of the heavy isotope of hydrogen in determining the type of catalysis.<sup>†</sup>

Probably the simplest example of saponification is that of the hydrogen molecule, which has been followed in alkaline solutions of D<sub>2</sub>O by Wirtz and Bonhoeffer.<sup>‡</sup> Without a detailed knowledge of the mechanism we would write the chemical equation in the conventional form



Isotopic analysis, however, proves the actual change to be



in agreement with the conclusion (p. 136) reached from the use of a heavy isotope of oxygen in the alkaline saponification of esters, and from the earlier general arguments of Lowry (p. 317).

### *Exchange Reactions*

In the preceding section we have compared the rates and energies of activation of some reactions involving H with the corresponding quantities for the reactions involving D. We have here to discuss the rate of exchange of an atom forming part of a solute molecule with its isotope in the solvent, which is generally a hydroxylic medium.

Most of the work in this field has been confined to the exchange of hydrogen with its heavy isotope. The hydrogen atom attached to the carbon atom in a solute as a rule exchanges its place with a hydrogen atom in the solvent molecule only with difficulty. When, however, a carbonyl group, —CO, is contiguous to the —CH group, the exchange is comparatively easy.<sup>§</sup> This fact at once suggests that the mechanism of exchange in this case is the keto-enol one, a view which is strengthened by the results|| summarized in Table 17. The parallelism between exchange and simple chemical reactions such as mutarotation and saponification is striking. Thus, reactions such as 3 and 8, which occur between ions and solute dipoles, have normal velocities. The apparent inefficiency of reactions 4 and 5 vanishes when correction is made for the temperature variation of the collision

† Cf. Halpern, *J. Chem. Physics*, **3**, 459, (1935); R. P. Bell, *Proc. Roy. Soc., A*, **154**, 297, (1938); Hornel and Butler, *Trans. Chem. Soc.*, 1361, (1938); Reitz, *Z. physikal. Chem., A*, **183**, 371, (1939).

‡ *Ibid., A*, **177**, 1, (1936).

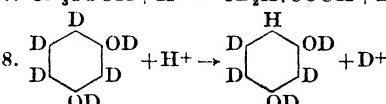
§ Bonhoeffer and Klar, *Naturwiss.*, **22**, 45, (1934).

|| Geib, *Z. physikal. Chem., A*, **180**, 211, (1937); Bok and Geib, *ibid., A*, **183**, 353, (1939).

frequency. A similar correction is probably needed in other cases, and the electrostatic repulsion between the reacting ions obviously enters into reactions 1 and 2.

By using the heavy isotope of oxygen ( $O^{18}$ ), I. Roberts and Urey† find the rate at which oxygen in the benzoate ion exchanges with

*Table 17*  
*The Arrhenius Constants for Certain Exchange Reactions in Aqueous Solution*

Reaction	$\log_{10} A$ ( $A$ in litres/gm. mole-sec., except for reactions 4 and 5, for which $A$ is in sec. <sup>-1</sup> )	$E_A$ (kilocalories per gm. mole)
1. $CH_3COO^- + DO^- \rightarrow CH_2D.COO^- + HO^-$	7.9	
2. $CD_3COO^- + HO^- \rightarrow CD_2H.COO^- + DO^-$	7.6	$22 \pm 2$
3. $CD_3COOH + HO^- \rightarrow CD_2H.COOH + DO^-$	11.7	
4. $CH_3COO^- + D_2O \rightarrow CH_2D.COO^- + HOD$	10.8	
5. $CD_3COO^- + H_2O \rightarrow CD_2H.COO^- + HOD$	10.5	$32 \pm 1$
6. $CH_3COOD + D^+ \rightarrow CH_2D.COOD + H^+$	9.1	
7. $CD_3COOH + H^+ \rightarrow CD_2H.COOH + D^+$	8.8	$26 \pm 1$
8. 	11.5	$20.5 \pm 0.7$

oxygen in the water used as solvent at 80° C. to be comparable with the velocity of esterification of benzoates in solutions containing the same concentration of catalyst (HCl). Over a fivefold range of catalyst concentration the observed unimolecular constant for the exchange reaction is proportional to [HCl], yielding a catalytic coefficient of  $2.37 \times 10^{-4}$  litres/gram mole-second, and showing no signs of a primary electrolyte effect. Moreover, both oxygen atoms of the carboxyl ion are exchanged, which, as the investigators point out, is consistent with their essential equivalence in the symmetrical ion.‡

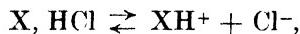
The heavy isotopes of both hydrogen and chlorine have been used by Nevell, de Salas, and C. L. Wilson§ in their study of the Wagner-Meerwin rearrangement in chloroform solution. The conversion of camphene hydrochloride into *isobornyl* chloride has been shown to

† *J. Amer. Chem. Soc.*, **61**, 2580, (1939).

‡ An earlier claim was that only one oxygen atom was readily replaceable—Koizumi and Titani, *Bull. Chem. Soc., Japan*, **13**, 607, (1938).

§ *Trans. Chem. Soc.*, 1188, (1939).

proceed in two stages, the first of which is a rapid establishment of the equilibrium



and the second of which is the rate-determining bimolecular reaction



The mechanism is consistent with the kinetic order of 3/2 established by Bartlett and Pöckel† for the rearrangement of the salt in the absence of added acid.

#### *A Quantitative Formulation of General Acid and Base Catalysis*

It is impossible to say in advance which reactions are catalysed only by hydrogen ions and which are catalysed by hydrogen ion, ammonium ion, water, and any other undissociated acid. For reactions catalysed by anything which can give a proton, Brönsted‡ found that the catalytic coefficient is related as follows to the dissociation constant of the proton-container:

$$k_A = \alpha K_A^\alpha. \quad (19)$$

$\alpha$  and  $\alpha$  are specific isothermal constants for the system. A corresponding relation

$$k_B = b K_A^{-\beta} \quad (20)$$

holds for basic catalysis, where  $K_A$  is the dissociation constant of the acid from which the base is formed. This empirical relation is illustrated logarithmically in Fig. 4, where  $n$  is an integer.§

To translate these relationships into the realm of energy|| we must assume, though without direct experimental support, that  $\alpha$  and  $\alpha$  in acid catalysis, and  $b$  and  $\beta$  in basic catalysis, are independent of temperature. Then

$$E_A = E_a + \alpha H_A \quad (21)$$

and

$$E_B = E_b - \beta H_A, \quad (22)$$

where  $E_A$ ,  $E_B$  stand for the Arrhenius energies of activation of the catalysed reactions,  $H$  for the increase in heat content attending the ionization of the acid, and  $E_a$ ,  $E_b$  are generic constants.

On applying relation (21) to catalysis by hydrogen ion, for which  $H_A$  is obviously zero, we see that  $E_a$  is in fact  $E_H$ , so that

$$E_A = E_H + \alpha H_A. \quad (23)$$

In words, the energy of activation for a reaction catalysed by an

† *J. Amer. Chem. Soc.*, **60**, 1585, (1938).

‡ *Chem. Rev.*, **5**, 231, (1928).

§ Brönsted and Pedersen, *Z. physikal. Chem.*, **108**, 195, (1924).

|| Moelwyn-Hughes, *Alembic Club Lecture*, Oxford, 13 October 1930.

undissociated acid exceeds the energy of activation of the same reaction catalysed by hydrogen ion by an amount which is proportional to the energy of dissociation of the acid. This fact is one that is very readily interpreted in terms of the general theory of the forces holding the proton to the water molecule and to other bases.†

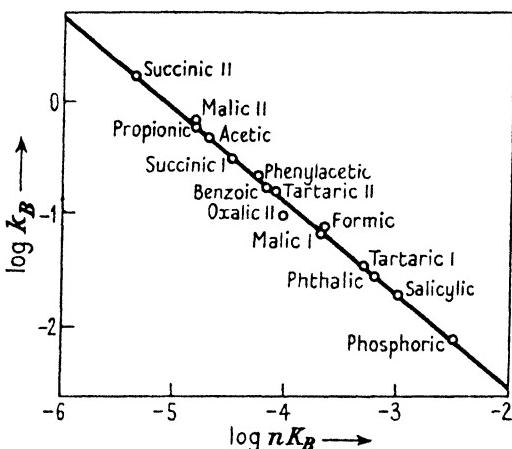


FIG. 4. General basic catalysis of the nitramide decomposition.

On applying relation (22) to catalysis by water molecules, for which  $H_A$  is again obviously zero, we see that  $E_b = E_W$ , so that

$$E_B = E_W - \beta H_A, \quad (24)$$

which is illustrated in Table 18 from data‡ on the enolization of acetoacetic acetate.

On combining equation (23) as applied to catalysis by hydrogen ion and water molecules, with equation (24) as applied to catalysis by hydroxyl ion and water molecules, we have the evident result:

$$\frac{E_H - E_{OH}}{H_W} = \beta - \alpha. \quad (25)$$

† Horiuti and Polanyi, *Acta Physicochim. U.S.S.R.*, **2**, 505, (1935); Moelwyn-Hughes, *ibid.*, **4**, 173, (1936). The numerical constants obtained by the late Dr. A. Sherman for the quantal relation cited in the latter work are:

$$E = 0.8D_1 - (0.75 - 0.00825\Delta H)D_2,$$

when  $D_1$  is the dissociation energy of the bond broken, and  $D_2$  that of the bond formed, in kilocalories/gm. mole. For fuller accounts see Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., p. 333, Oxford, (1941); Bell, *Acid-Base Catalysis*, Oxford, (1941).

‡ Pedersen, *J. Physical Chem.*, **38**, 1019, (1934).

But (Table 15) the ratio on the left is 0.44 for a number of reactions; hence, very roughly,  $(\beta - \alpha) \sim \frac{1}{2}$ . (26)

There are not sufficient data to test this relation, which depends on a number of assumptions still requiring substantiation. In general, however,  $\beta$  is known to be greater than  $\alpha$ . Two cases of interest arise. When  $\alpha = \frac{1}{2}$ ,  $\beta = 1$ , that is  $E_{OH} = E_b - H_w$ . Applied to the specific case examined by Pedersen, this leads to a value of almost zero for the reaction as catalysed by hydroxyl ions. Secondly, when  $\beta = \frac{1}{2}$ ,  $\alpha = 0$ , that is, there is no acid catalysis. We may therefore predict that  $\beta$  is not far off 0.5 for reactions which, like the catalytic hydrolysis of trichloracetic esters, are insensitive to hydrogen ions.

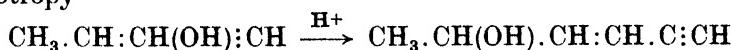
Table 18

*Energetics of the Base-catalysed Enolization of an Acetoacetic Ester*

Catalyst	$E_B$	$E_w - \beta H_A$
$CH_3COO^-$	13,400	13,500
$CH_3OHCOO^-$	13,100	13,600
$CH_3ClCOO^-$	13,800	(13,800)
$H_2PO_4^-$	14,000	13,000
$SO_4^-$	17,500	13,700
$H_3O$	14,200	14,200

*The Influence of the Dielectric Constant of the Medium on Catalysis*

Attention has been drawn (p. 279) to the influence of the dielectric constant of the solvent on the rate of mutarotation of glucose. Amist has also examined the inversion of cane sugar in mixed hydroxylic solvents. Most of the solvents used in acid catalysis are mixtures of alcohol and water, in which, when the rate of reaction is plotted as a function of the solvent composition, are invariably found the familiar minima near the alcohol end. The decrease in catalytic efficiency can only be in part attributable to the replacement of  $H_3O^+$  by  $C_2H_5O^+$ , and some influence due to the medium must be included. The following interesting example‡ of a purely aliphatic anisotropy



has been measured in solvents of various compositions,§ and it is found that the energy of activation, corrected for the electrostatic

† *J. Amer. Chem. Soc.*, **63**, 2231, (1941).

‡ E. R. H. Jones and McCombie, *Trans. Chem. Soc.*, **261**, (1943).

§ E. R. H. Jones, *ibid.*, **436**, (1944); Braude, *ibid.*, **443**, (1944).

effect, is constant at  $30.6 \pm 0.9$  kilocalories, while the apparent energy of activation,  $E_A$ , is about 4 times as variable.

Murphy† has determined the apparent energy of activation,  $E_A$ , for the decomposition of diacetone-alcohol under the catalytic influence of the hydroxyl ion in mixtures of ethyl alcohol and water. On plotting  $E_A$  against  $1/D$ , we find an approximate value of 24 kilocalories for the reaction in pure alcohol, and  $dE_A/d(1/D)$  to be about 400 kilocalories. The latter figure, by the method shown in Chapter V, leads to the not impossible value of 0.07 for  $\mu \cos \theta/r^2$ . The electrostatic component of the energy of activation, however, may not be simply proportional to  $1/D$ , but to some more elaborate function of  $D$ , as illustrated in Chapter VII.

### *Negative Catalysis*

Just as a positive catalyst can accelerate a reaction in many ways, a negative catalyst can retard it in many ways. Since small amounts of a catalyst can produce a marked increase in the rate, a small amount of any substance which will destroy or incapacitate the catalyst can produce a marked decrease in the velocity. Examples will be cited in Chapter XII, when dealing with catalytic poisons. The retarding influence of a negative catalyst upon the rate of an uncatalysed reaction cannot be understood in this way, and other hypotheses are necessary. Two of these may be mentioned here. When a reaction proceeds by a chain mechanism, any substance which interrupts a single process in the chain can produce a considerable damping of the velocity by prematurely terminating a chain which would otherwise have involved many cycles. Secondly, a negative catalyst may function by combining with the reactant to form a complex which is more resistant to chemical change than is the uncombined reactant. Instances of both types of negative catalysis are known.

Explosive reactions are obviously less likely to occur in solution than in the gas. Sealed samples of solutions of chlorine monoxide in carbon tetrachloride, of ozone in hexane, and even of alkyl halides in water have been known to blow up. Yet there is no direct evidence for the existence of explosions in solution, for the question is experimentally difficult to settle, since solutions are usually examined in the presence of a vapour phase.

† *Loc. cit.*

The experimental investigation of negative catalysis in solution was first approached in a comprehensive manner by Titoff.<sup>†</sup> Sodium sulphite in aqueous solution is oxidized by atmospheric oxygen, the velocity being unimolecular with respect to the sulphite. The most significant feature of the reaction is the marked inhibitive effect produced by the addition of minute quantities of a variety of substances such as salts of manganese and chromium, mannite, aniline, potassium cyanide, and numerous alkaloids.<sup>‡</sup> That reaction proceeds by a chain mechanism was proved by Bäckström,<sup>§</sup> who confirmed the earlier work on the inhibition by various substances, particularly alcohols, and found the rate of reaction to be given by an equation of the form

$$\text{rate} = \frac{k_1}{kC + k_2}, \quad (27)$$

which is based on equation I (51), and resembles equation VIII (38).  $C$  is the concentration of inhibitor, and  $k_1$ ,  $k$ , and  $k_2$  are constants,  $k$  depending upon the nature of the inhibitor. The relative values of  $k$  are—mannite:methyl alcohol:ethyl alcohol:benzyl alcohol::1:0.5:1.3:60. They demonstrate the varying chain-breaking efficiency of the different alcohols, each of which is destroyed by the change which it inhibits.<sup>||</sup> Bäckström measured the length of the chains by assuming that, when inhibition is considerable, all the chains are broken by molecules of the inhibitor. The number of alcohol molecules destroyed in unit time gives the number of chains terminated in unit time, and, since the chains are stationary, the number initiated in unit time. The total number of sulphite molecules oxidized, when divided by the number of chains, gives the average number of links in each chain. When sodium sulphite is oxidized in aqueous solution, about 50,000 molecules are converted for each initial act. The chain is of remarkable length. Comparable figures were found also for the oxidation of benzaldehyde (10,000) and heptaldehyde (15,000).

The interpretation is confirmed by measurements of the photochemical oxidation. The velocity is increased by light of appropriate frequency, and is given by the same relation as for the dark reaction, multiplied by a new constant  $k_3$  which is the ratio of the velocities of the photochemical and thermal reactions. The quantum efficiencies

<sup>†</sup> *Z. physikal. Chem.*, **45**, 641, (1903).

<sup>‡</sup> Young, *J. Amer. Chem. Soc.*, **24**, 297, (1902).

<sup>§</sup> *Loc. cit.*

<sup>||</sup> Inhibitors can break the chain without themselves undergoing chemical change.

of the photochemical changes are 50,000, 10,000, and 15,000, which shows that the chain-length is not altered. In the photochemical oxidation the number of chains initiated is greater than in the thermal reaction, but the mechanism of reaction is the same.

Further investigations† have shown that the inhibitory action is connected with the induced oxidation of the alcohols. The oxidation of benzaldehyde is inhibited also by anthracene, which during the reaction is itself converted by induced oxidation to anthraquinone.‡ The active agent, which is identified as a peroxide, suffers at least 1,000 collisions with benzaldehyde molecules before finally giving up its energy. These observations are readily formulated in terms of equation I (51), extended to account for the additional deactivations due to added solutes, and applied to conditions governing a net pseudo-unimolecular change.§

The alternative explanation of negative catalysis receives support from the large volume of work which has accumulated on the inhibitive action of water and other substances upon the velocity of decomposition of organic acids in sulphuric acid solution.|| One example may be considered in detail—the quantitative conversion of malic acid into  $\alpha$ -pyrone- $\beta'$ -carboxylic acid, with water and carbon monoxide, the latter providing a suitable means for manometric estimation.†† The reaction in pure sulphuric acid presents no novel features,  $k$  being unimolecular and given accurately by the equation  $k = 1.78 \times 10^{15} e^{-25330/RT}$ . Ten substances of widely different character inhibit the reaction, which has been measured in the presence of varying amounts of each at three temperatures. Dittmar interprets the results in terms of a reactive complex of malic acid and sulphuric acid, the existence of which is confirmed by solubility measurements. The inhibitors act by combining with malic acid and thus diminishing the concentration of the reactive complex.

Dittmar's results may be examined in the following way by a study of the observed critical increments under each set of conditions. In

† Alyea and Bäckström, *J. Amer. Chem. Soc.*, **51**, 90, (1929).

‡ Bäckström and Beatty, *J. Physical Chem.*, **35**, 2530, (1931).

§ Jeu and Alyea, *J. Amer. Chem. Soc.*, **55**, 575, (1932).

|| Oxalic acid, Lichtry, *ibid.*, **11**, 225, (1907); formic acid, Meyer, *Z. Elektrochem.*, **15**, 506, (1909); succinic acid, Wiig, *J. Amer. Chem. Soc.*, **52**, 4742, (1930); malic acid, Whitford, *ibid.*, **47**, 953, (1925).

†† Dittmar, *ibid.*, **47**, 987, (1925); **52**, 2746, (1930). For the kinetics of the decomposition, in sulphuric acid solutions, of triphenyl acetic acid into carbon monoxide and triphenylcarbinol, see Dittmar, *J. Phys. Chem.*, **33**, 533, (1929).

seven cases, the second addition of the inhibitor causes an average increase in  $E_A$  of 490 calories. The factor  $e^{\Delta E/RT}$  is 2·3, which accounts

Table 19  
*The Energetics of Negative Catalysis*

Inhibitor	$E_A$		
	No inhibitor	0·25 mol. of inhibitor	0·50 mol. of inhibitor
Ammonium sulphate		27,640	28,240
Phenol		27,640	29,310
<i>p</i> -Cresol		27,380	28,030
Coumarin		27,900	28,120
Benzophenone	25,330	26,980	27,340
Benzoic anhydride		30,400	31,060
Ethyl alcohol		26,800	26,470
Benzoic acid		27,160	27,160
<i>ortho</i> -Phosphoric acid		26,890	27,470
Acetophenone		26,900	26,050

almost exactly for the decrease in velocity corresponding to the second addition. The interpretation given by Dittmar seems therefore to be justified. It is a special application of the intermediate-complex theory, exhibiting a rather unusual phenomenon which is of some importance. When, as in most of the studies hitherto encountered, the intermediate complex is more reactive than the uncombined reactant, there is a fall in  $E_A$ , the extent of the fall being independent of the amount of catalyst. In the present case,  $E_A$  rises with the addition of the negative catalyst, successive additions causing a continual increase. The reason for this is not far to seek. With a positive catalyst, two simultaneous reactions occur side by side, but usually the catalytic coefficient is so much greater than the uncatalysed reactivity that the latter becomes negligible in comparison.  $E_A$  therefore gives the heat of activation of the catalysed reaction. With a negative catalyst, also, there are at least two simultaneous reactions, and since the inhibitive effect is often less marked than a catalytic effect, the velocity of the uninhibited reaction is usually comparable with that of the inhibited one, especially with small amounts of negative catalysts. The true  $E$  for the inhibited reaction cannot be evaluated until sufficient of the negative catalyst has been added to remove nearly all of the uncombined reactant. It will be noticed from the table that the first addition of inhibitor causes  $E_A$  to rise by about 2,500 calories: the second addition causes  $E_A$  to rise a

further 500 calories only, so that the conditions are quickly approximating to those of a completely inhibited reactant. Inhibition in this case is strictly a misnomer. The slow reaction which is measured is really the decomposition of another substance. In true inhibiting effects, the chemical change which is measured is the same in the presence of all inhibitors.

Dittmar's explanation does not apply to Bäckström's results, but Christiansen's theory may be able to interpret Dittmar's. As in positive catalysis, so in negative catalysis, the variety of phenomena calls for a variety of hypotheses, all of which may find justification under special circumstances.

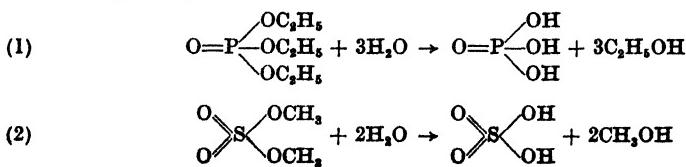
### *Discussion*

The term catalysis has a definite content, but the term catalyst has not. Cyanomethane, a catalyst towards the Beckmann rearrangement of certain oximes, inhibits other reactions. Catalysis, in other words, is essentially an interaction phenomenon, and no chemical compound can claim to be a catalyst.

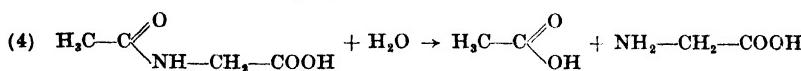
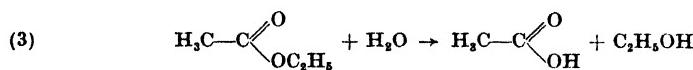
Some changes, previously designated as catalytic, are now known to be chemical reactions proper; the catalyst undergoes chemical combination at one part of the reacting molecule, while it, in its turn, discharges another unit of the so-called catalyst from its other end. Tracer work has, in short, removed many supposed catalyses into the category of chemical changes.

The fact that iodine atoms and molecules in the gas phase and iodine atoms and ions in solution have catalytic powers towards certain reactions suggests that a wealth of electrons, and a consequent high polarizability and range of electronic vibration frequencies, endows them with catalytic efficacy. Such an argument, however, is nullified by the fact that the proton, which possesses none of these properties, is a good catalyst in certain hydrolyses, though not in all, as the following examples show:

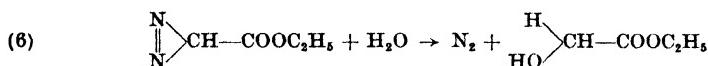
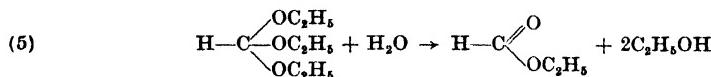
#### *Not catalysed by hydrogen ions:*



*Catalysed by hydrogen ions:*



*Powerfully catalysed by hydrogen ions:*



We are led back to the essential idea of catalysis as energetic interaction, which in these specific cases would appear to be connected with a contiguity in the ester molecule of a C—H group to the group awaiting cleavage.

Optical dispersion may be thought of as catalysis, by the electrical component of light, of the process of ionization of the refracting molecules.<sup>†</sup> Polar catalysis can then be quantitatively formulated as an increase in the tendency of the reacting molecule towards ionic cleavage.

<sup>†</sup> See Moelwyn-Hughes, *Physical Chemistry*, p. 107, Cambridge, (1940).

## XI

## THE VARIATION OF REACTION VELOCITY WITH RESPECT TO PRESSURE

BECAUSE of the complexity of liquids, and the still greater complexity of solutions, it is not at present possible to predict how the application of external pressure may influence the velocity of reaction in either of the condensed fluid states. Some baffling results were obtained in the earliest work carried out in this field. Thus, the rate of hydrolysis of sucrose by acetic acid, and the rates of hydrolysis of esters by acids<sup>†</sup> and alkalis<sup>‡</sup> were found to increase by about 25 per cent. when an external pressure of 1,000 atmospheres was applied. To render the evidence inconclusive, however, the catalytic effect of strong acids on the inversion was found to be an adverse one.<sup>§</sup> Within recent years interest in this branch of chemical kinetics has greatly revived, with the result that the problem, though still unsolved, can now be more fairly posed.

### *Van 't Hoff's Theory*

The general theory of the effect of pressure on the velocity of chemical change was first propounded by van 't Hoff,<sup>||</sup> whose treatment, very largely overlooked, may now be reproduced, using a newer notation.

Consider the chemical equilibrium represented by the equation



The equilibrium constant,  $K$ , is defined by either of the following equations

$$K = \frac{[AB]}{[A][B]} = \frac{k_2}{k_1}, \quad (2)$$

where the bracketed terms denote activities and the  $k$  terms velocity coefficients. We employ the thermodynamic relations

$$\Delta G^0 = -RT \ln K \quad (3)$$

and  $\Delta G^0 = \Delta E^0 + P\Delta V^0 - T\Delta S^0,$  (4)

<sup>†</sup> Rothmund, *Z. physikal. Chem.*, **20**, 168, (1896).

<sup>‡</sup> Cohen and Kaiser, *ibid.*, **89**, 338, (1915); Walker, *Proc. Roy. Soc., A*, **78**, 157, (1907).

<sup>§</sup> Röntgen, *Annalen*, **45**, 98, (1892); Cohen and de Boer, *Z. physikal. Chem.* **84**, 41, (1913).

<sup>||</sup> *Vorlesungen über theoretische und physikalische Chemie*, 1, p. 236, Braunschweig, (1901).

in which  $G$  stands for the Gibbs function,  $E$  for the internal energy,  $V$  for the volume,  $S$  for the entropy, and  $\Delta$  for the excess of the molar property possessed by the products over that possessed by the reactants when each is in some convenient reference state. On combining the two formulae, we obtain

$$\ln K = -\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} - \frac{P\Delta V^0}{RT}. \quad (5)$$

Differentiation with respect to pressure at constant temperature then yields the expression

$$\left(\frac{d \ln K}{dP}\right)_T = -\frac{\Delta V^0}{RT}. \quad (6)$$

Reactions which are attended by an increase in volume ( $\Delta V^0$  is positive) are therefore impeded by an increase in pressure, and *vice versa*. Equation (6) is, therefore, but a quantitative formulation of le Chatelier's principle in its bearing on our immediate problem. Van 't Hoff† found it to be in satisfactory agreement with experimental values of the pressure coefficient of the electromotive force of reversible cells.

Now, by definition,  $\Delta V^0$  is the difference between the volume,  $V_2$ , of the products and the volume,  $V_1$ , of the reactants:

$$\Delta V^0 = V_2 - V_1. \quad (7)$$

This equation may also be written as follows:

$$\Delta V^0 = (V_2 - V_c) - (V_1 - V_c), \quad (8)$$

in which  $V_c$  is an arbitrary volume. On combining equations (2), (6), and (8), we see that

$$\left(\frac{d \ln k_2}{dP}\right)_T - \left(\frac{d \ln k_1}{dP}\right)_T = -\frac{(V_c - V_1)}{RT} + \frac{(V_c - V_2)}{RT}. \quad (9)$$

The resolution of this equation into two separate equations, one purporting to hold for the forward and one for the reverse reaction, is equivalent to giving  $V_c$  a unique, as distinct from an arbitrary, value, and is a pure assumption which can only be justified *a posteriori*. Van 't Hoff intuitively regarded the assumption as a reasonable one, and thus arrived at the relations:

$$\left(\frac{d \ln k_2}{dP}\right)_T = -\frac{(V_c - V_1)}{RT} \quad (10)$$

$$\text{and} \quad \left(\frac{d \ln k_1}{dP}\right)_T = -\frac{(V_c - V_2)}{RT}. \quad (11)$$

† *Loc. cit.*

In general, we may therefore write

$$\left( \frac{d \ln k}{dP} \right)_T = -\frac{(V_c - V)}{RT} = -\frac{\Delta V_c}{RT}. \quad (12)$$

This relation implies that the velocity coefficient of a chemical reaction increases with increasing pressure, when the volume,  $V_c$ , of the active molecules is less than the volume,  $V$ , of the reactants. If, on reacting, a molecule must pass through a more voluminous state, its velocity of reaction will be adversely affected by pressure. It will be shown later that the velocities of most chemical changes are favourably influenced by pressure. We therefore conclude that, for the majority of reactions in solution, the active molecules form a more compact structure than the passive molecules.<sup>†</sup>

In the examples investigated by Moesveld,<sup>‡</sup> the magnitude of the pressure effect was found to be independent of the temperature, and, although this observation cannot be generalized, it is one which has since been found to hold for a variety of reactions. When such a condition prevails we may integrate equation (12), and obtain the simpler relation

$$k_P = k_0 e^{-P \Delta V_c / RT}. \quad (13)$$

Here  $k_P$  is the velocity coefficient when the reacting system is under an external pressure  $P$ , and  $k_0$  the velocity coefficient in the absence of external pressure.

Just as the critical increment of energy, which differentiates active from passive molecules, can be measured by examining the variation of the velocity coefficient with respect to temperature, the critical increment of volume, which is the difference between the volume of the active and passive molecules, can be found by studying the variation of the velocity coefficient with respect to pressure.

It has been suggested<sup>§</sup> that  $\Delta V_c$  relating to reactions in solution may be resolvable into components made up independently by solute and solvent.

#### *The Application of van 't Hoff's Theory to Reactions Catalysed by Hydrogen Ions in Aqueous Solution*

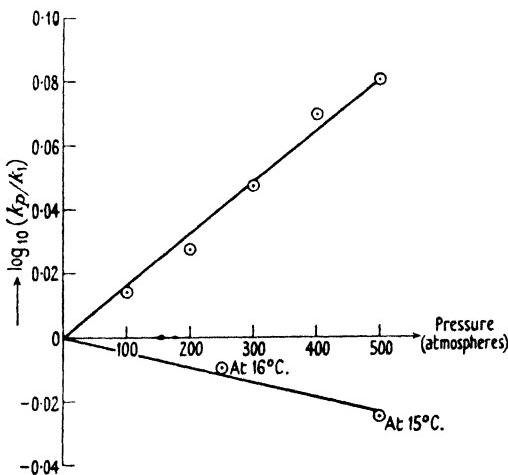
The pioneer experimental work (p. 338), though restricted to pressures not exceeding 500 atmospheres, suffices to establish the order of magnitude of the pressure effect and to afford a test of

<sup>†</sup> These adjectives are used in the sense originally given them by Arrhenius.

<sup>‡</sup> Z. physikal. Chem., 103, 486, (1923).

<sup>§</sup> M. G. Evans and Polanyi, Trans. Faraday Soc., 31, 875, (1935).

van 't Hoff's treatment. In Fig. 1 we have plotted the results of Rothmund† relating to the hydrolysis of methyl acetate and sucrose in *N*-hydrochloric acid solution. The logarithm of the catalytic coefficient, relative to its value at atmospheric pressure, is shown as ordinate, and the pressure exerted on the system as abscissa. From



Upper curve: The hydrolysis of methyl acetate, catalysed by *N*-hydrochloric acid at 14° C.

Lower curve: The hydrolysis of sucrose, catalysed by *N*-hydrochloric acid.

FIG 1. The influence of pressure on the velocity of catalysed hydrolyses in aqueous solution.

the gradient, it is found that  $\Delta V_c$  is  $-8.7$  c.c./gram mole in the hydrolysis of the ester, and  $+2.5$  c.c. in the inversion of cane sugar (these are slight revisions of the first estimates,‡ which were  $-9.0$  and  $+2.7$  c.c.). A comparison of the experimental results with those reproduced by equation (13) is to be found in Table 1. The numerical agreement, to within the seldom found limits of  $\pm 1$  per cent., is excellent. An external pressure of 500 atmospheres is seen to increase the rate of hydrolysis of the ester by 21 per cent., and to decrease the rate of hydrolysis of sucrose by 6 per cent. Impressed by the difference in the sign and magnitude of the pressure effect on these two hydrolytic processes under comparable conditions, one may be tempted to anticipate a close connexion between the present differentiation and an earlier one based on the absolute magnitude of the velocity

† Loc. cit.

‡ Moelwyn-Hughes, *Trans. Faraday Soc.*, **32**, 1723, (1936).

coefficient. It will be recalled that the ester hydrolysis belongs to the category of slow reactions, and the sugar hydrolysis to the category of fast reactions. It would, in fact, not be unreasonable to expect reactions with normal velocities to be uninfluenced by pressure changes. Such an anticipation, however, is not realized, although, as we shall see, subsequent work has shown that pressure has less effect on bimolecular reactions proceeding with normal velocities than it has on fast or slow reactions. Some doubt may be entertained as to whether any chemical change can be absolutely independent of the pressure: so long as molecules insist on absorbing energy before undergoing chemical reaction, they must, in general, alter their configuration, which can seldom be achieved without a change in volume, even if the activation energy is accommodated electronically. However that may be, it is still true to say, as van 't Hoff first said, that the reactions most suited to test the influence of pressure on the rate are isomerisms. No work has, unfortunately, been done in this field. The catalytic mutarotation of glucose by ions, and, provided we make allowance for the variation of collision frequency with temperature, by molecules also, fit in perfectly with the elementary notion of conversion during every activated collision, and it is possible that  $\Delta V_c$  in this case would be so small as to elude measurement.

Table 1

*The Influence of Pressure on Hydrolyses Catalysed by N-Hydrochloric Acid in Aqueous Solution*

Reaction	Tempera- ture (°C.)	Pressure (atmo- spheres)	$k_p/k_0$	
			Obs.	Calo.
The hydrolysis of 5 per cent. methyl acetate ( $\Delta V_c = -8.7$ c.c.)	14	1	1.00	1.00
	14	100	1.03	1.04
	14	200	1.07	1.08
	14	300	1.12	1.12
	14	400	1.17	1.16
	14	500	1.21	1.20
The hydrolysis of 20 per cent. sucrose in water ( $\Delta V_c = +2.5$ c.c.)	16	1	1.00	1.00
	16	250	0.98	0.97
	15	500	0.94	0.95

As an illustration of the use to which equation (8) may be put, we may briefly consider the inversion of cane sugar, for which we have found a value of  $+2.5$  c.c. for  $\Delta V_c$ . The reactive complex in this

case must have a greater volume than the ordinary reactants—a conclusion which agrees with our knowledge of structural organic chemistry,† according to which the hydrolysis of sucrose entails the opening of a furanose ring and a subsequent closing into a pyranose ring. From the data of Fresenius‡ it may readily be shown that the total dilatometric change,  $\Delta V^0 = V_2 - V_1$ , accompanying the hydrolysis of one gram mole of sucrose at 15° C. is +1.9 c.c. It follows from equation (8) that  $V_2 - V_c$  is +0.6. Hence the synthesis of the disaccharide from the two hexoses must also be subject to a slight adverse pressure effect. These elementary considerations are depicted in Fig. 2. When reactions proceed with a net decrease in volume, the right limb depends lower than the left one.

### *The Influence of Pressure on the Velocity of Esterification in the Liquid State*

The rate at which an aliphatic acid reacts with an aliphatic alcohol when they are mixed at ordinary temperatures and pressures is very slow, but it may be hastened by increasing the temperature or the pressure. The kinetics of the formation of acetates from equimolar mixtures of acetic acid and a number of primary and secondary aliphatic alcohols has been the subject of an investigation by Shu-lin P'eng, Sapiro, Linstead, and Newitt,§ from whose work the figures and tables of this section are taken.

It will be observed (Fig. 3) that in all cases the logarithm of the velocity of reaction is linearly related to the pressure within the region examined, which extends to 4,000 atmospheres. From the gradients of these curves are found the critical volume decreases shown in Table 2.

The constants  $A$  and  $E_A$  of the Arrhenius equation have the values summarized in Table 3. The rate of formation of ethyl acetate is seen to increase by a factor of about 24 when the pressure is altered from one atmosphere to 4,000 atmospheres. The constant  $A$  is found

† W. N. Haworth, *The Constitution of the Sugars*, Arnold, (1929); E. F. and K. K. Armstrong, *The Glycosides*, 2nd ed., Longmans, (1933).

‡ Landolt-Börnstein's *Physikalisch-chemische Tabellen*.

§ *Trans. Chem. Soc.*, 784, (1938).

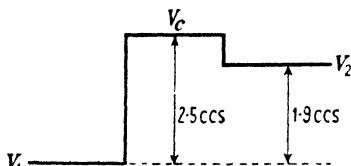


FIG. 2. Diagrammatic representation of the initial, the critical, and the final volumes in the hydrolysis of sucrose at 15° C.

to increase by a factor of 35. The greater influence of pressure thus seems to be felt on  $A$  rather than on  $E_A$ , which may be construed

Table 2

*Values of  $-\Delta V_c$  (or  $V_1 - V_c$ ) for Esterification Reactions, in c.c./gm. mole*

Alcohol	Temperature (°C.)		
	70°	75°	80°
Ethyl	22.48	23.35	—
<i>n</i> -Propyl	19.70	20.03	20.39
<i>n</i> -Butyl	18.44	18.94	19.50
<i>iso</i> -Propyl	18.90	20.45	21.47
<i>iso</i> -Butyl	13.70	14.23	14.84
<i>sec</i> .-Butyl	22.20	22.00	24.40

Table 3

*Values of the Constants of the Arrhenius Equation for the Rate of Esterification of Acetic Acid with a series of Alcohols*

Alcohol	Pressure (atmo- spheres)	$E_A$ (calories/gm. mole)	$A$ (litre/gm. mole-sec.)
Ethyl	1	13,770	$4.58 \times 10^2$
	2,000	13,790	$2.40 \times 10^3$
	3,000	13,830	$6.10 \times 10^3$
	4,000	13,980	$1.61 \times 10^4$
<i>n</i> -Propyl	1	13,550	$4.10 \times 10^2$
	2,000	13,910	$2.98 \times 10^3$
	3,000	14,190	$8.87 \times 10^3$
	3,750	14,740	$3.33 \times 10^4$
<i>n</i> -Butyl	1	13,720	$5.69 \times 10^2$
	2,000	14,580	$7.00 \times 10^3$
	3,000	14,950	$2.44 \times 10^4$
	3,750	15,190	$5.72 \times 10^4$
<i>iso</i> -Propyl	1	15,890	$3.20 \times 10^3$
	2,000	19,400	$2.15 \times 10^6$
	3,000	20,660	$2.66 \times 10^7$
	3,750	22,220	$4.38 \times 10^8$
<i>iso</i> -Butyl	1	16,480	$4.84 \times 10^4$
	2,000	17,850	$1.30 \times 10^6$
	3,000	18,240	$3.35 \times 10^6$
	3,750	18,780	$1.16 \times 10^7$
<i>sec</i> .-Butyl	1	17,460	$2.50 \times 10^4$
	2,000	19,790	$3.53 \times 10^6$
	3,000	21,010	$4.90 \times 10^7$
	3,750	21,720	$2.22 \times 10^8$

as meaning that pressure primarily affects the rate by increasing the frequency of collisions. This conclusion, however, is not supported by the data for the other systems examined, from which it

is evident that both constants of the Arrhenius equation are affected (see Fig. 4). These results furnish yet another instance of  $A$  increasing steadily as  $E_A$  increases.<sup>†</sup>

When the components of an equimolar liquid mixture react bimolecularly, as in the present case, we infer that the type of collision

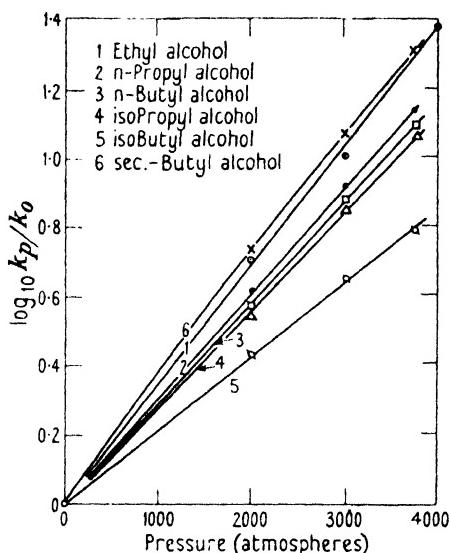


FIG. 3.

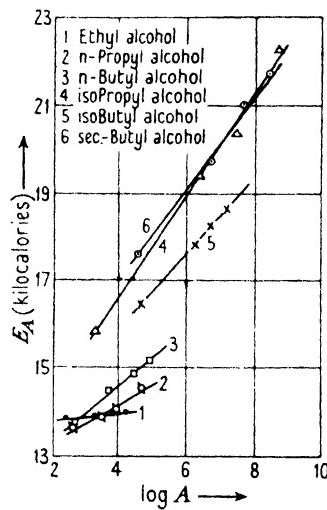


FIG. 4.

FIG. 3. Verification of equation (12) in the case of the reaction of equimolar mixtures of acetic acid with various alcohols.

FIG. 4. The variation of the constants  $E_A$  and  $A$  at various pressures for reactions of the type  $\text{CH}_3\text{COOH} + \text{ROH} \rightarrow \text{CH}_3\text{COOR} + \text{H}_2\text{O}$ .

is the solute-solvent kind, the frequency of which, according to equation IX (5), is proportional to the viscosity. The viscosities of the mixtures examined are not known, but complete data are available<sup>‡</sup> for the various alcohols. The viscosity of normal butyl alcohol at 75° C. has been found by Bridgman to be 3.50 times as great at 2,000 atmospheres as at 1 atmosphere at 75° C. The velocity of esterification by acetic acid at the same temperature is increased by a factor of 3.97. As far as it goes, this is evidence in favour of regarding the principal effect of pressure as due to its effect on the viscosity, to which, according to our supposition, the collision frequency is proportional. Other viscosity data at high pressures,

<sup>†</sup> *Chem. Rev.*, **10**, p. 260, (1932).

<sup>‡</sup> Bridgman, *The Physics of High Pressures*, Bell, London, (1931).

however, are necessary before a clear-cut decision can be reached, as Shu-lin P'eng, Sapiro, Linstead, and Newitt† have pointed out.

### *The Influence of Pressure on the Viscosity of, and the Velocity of Reactions in, Solution*

According to equation (28) of Chapter I the velocity of reactions which involve collisions between molecules of solute and molecules of solvent is directly proportional to the viscosity of the medium. Reasons have been given for regarding the inversion of cane sugar, catalysed by hydrogen ions, as belonging to this class of reaction. Because the structure of one of the reactants resembles that of the solvent, we have the following expression for the frequency of binary collisions:

$${}_A Z_B = \frac{3\pi\eta}{4} \frac{n_A n_B}{n_S} (r_A + r_B) \left( \frac{1}{m_A} + \frac{1}{m_B} \right), \quad \text{I (30)}$$

to which the velocity of reaction may be expected to be proportional. Any factor influencing the viscosity should thus influence the reaction velocity. This supposition can be tested in connexion with the hydrolysis of sucrose, by combining the kinetic data to which reference has been already made with the later and more extensive data of Cohen and Valeton,‡ again using viscosity data interpolated from Bridgman's monograph. There is, on the whole, a quite striking parallelism (Table 4) between the relative viscosity and the relative

*Table 4*

*A Comparison of the Relative Viscosities of Aqueous Solutions of Cane Sugar under Pressure with the Relative Velocities of Inversion*

<i>P</i> (atmo- spheres)	At 15° C.		At 25° C.		At 35° C.		At 45° C.	
	$\eta_P/\eta_1$	$k_P/k_1$	$\eta_P/\eta_1$	$k_P/k_1$	$\eta_P/\eta_1$	$k_P/k_1$	$\eta_P/\eta_1$	$k_P/k_1$
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
500	0.96	0.94	1.01	1.02	1.03	1.03	1.03	1.04
1,000	—	—	1.04	1.05	1.05	1.06	1.06	1.06
1,500	—	—	1.07	1.05	1.07	1.06	1.08	1.06

velocity, extending even to that complicated region in the structure of water where high pressures diminish the viscosity. If, therefore, we may, following the argument given on p. 216, express the velocity

† *Loc. cit.* The last term in the differential equation given in this paper is an obvious misprint for  $(dV/dT)_P$ .

‡ *Z. physikal. Chem.*, 92, 433, (1918).

of reaction at a constant temperature as a function of the viscosity raised to an integral ordinal number, that number is one in the case of the inversion of cane sugar. The apparently limiting effect of pressures observed by Cohen and Valemont may be not unconnected with their use of acetic acid as a catalyst. The density correction is also an improvement, as  $kn_s/\eta$  is slightly less variable than  $k/\eta$  (Table 5) at high pressures.

Table 5

*The Relative Velocity of Inversion of Cane Sugar, compared with the Relative Viscosity of Water, at Various Pressures*

$P$ (atmospheres)	$(k_P/k_1)_{45^\circ}$	$(\eta_P/\eta_1)_{45^\circ}$	$(n_P/n_1)_{50^\circ}$	$\frac{(kn_s/\eta)_P}{(kn_s/\eta)_1}$	$\frac{(k/\eta)_P}{(k/\eta)_1}$
1	1.000	1.000	1.000	1.000	1.000
500	1.041	1.027	1.021	1.034	1.014
1,000	1.064	1.055	1.039	1.047	1.009
1,500	1.064	1.081	1.056	1.040	0.985
					Average $1.002 \pm 0.012$

### *The Effect of Pressure on a Variety of Reactions in a Variety of Solvents*

Still higher pressures have been attained by Gibson, Fawcett, and Perrin,<sup>†</sup> and by Williams, Perrin, and Gibson<sup>‡</sup> in their investigations of reactions carefully selected to represent the normal and slow types (p. 72). We have plotted some representative results in Fig. 5 from which it is seen that equation (12) appears to be obeyed by all reactions up to pressures of about 3,000 atmospheres, and by some reactions up to pressures of 8,000 atmospheres. Beyond this region, however, there is a marked flattening of the  $\ln(k_P/k_1)-P$  curve, as has been found by Bridgman for so many of the physical properties of liquids.<sup>§</sup> The only reaction among those examined whose rate is diminished by an increase in pressure is the unimolecular decomposition of methyl-allyl-phenyl-benzyl-ammonium bromide.

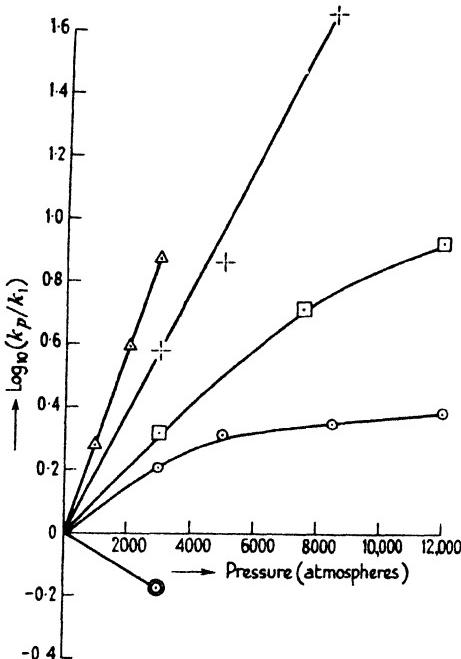
As an example of the applicability of equation (13), we have evaluated  $\Delta V_c$  for the reaction between acetic anhydride and ethyl alcohol in toluene solution at 40° C. as -11.45 c.c., which, as is seen from Table 6, reproduces the experimental values satisfactorily. Values of  $\Delta V_c$  which we have similarly obtained from the data of

<sup>†</sup> Proc. Roy. Soc., A, 150, 223, (1935).

<sup>‡</sup> Ibid., 154, 684, (1936).

<sup>§</sup> Bridgman, Rev. Mod. Physics, 18, 1, (1946).

Gibson, Fawcett, Perrin, and Williams† have been summarized in Table 7. Where there is divergence from the behaviour predicted by equation (12), initial gradients have been used. Table 7 also contains



1.  $\Delta$   $(\text{CH}_3\text{CO})_2\text{O} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{CH}_3\text{COOH}$  in  $\text{C}_6\text{H}_5\text{OH}$  at  $20^\circ\text{ C}$ .
2.  $+$   $(\text{CH}_3\text{CO})_2\text{O} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{CH}_3\text{COOH}$  in  $\text{C}_6\text{H}_5\text{CH}_3$  at  $40^\circ\text{ C}$ .
3.  $\square$   $\text{CH}_2\text{Cl}_2 + \text{NaOH} \rightarrow \text{CH}_2\text{OH} + \text{COONa} + \text{HCl}$  in  $\text{H}_2\text{O}$  at  $40.05 \pm 0.05^\circ\text{ C}$ .
4.  $\odot$   $\text{C}_2\text{H}_5\text{I} + \text{C}_2\text{H}_5\text{ONa} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{NaI}$  in  $\text{C}_2\text{H}_5\text{OH}$  at  $25.1 \pm 0.1^\circ\text{ C}$ .
5.  $\circledcirc$   $(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_3)(\text{CH}_3)(\text{C}_3\text{H}_5)\text{NBr} \rightarrow (\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_3)(\text{CH}_3)\text{N} + \text{C}_6\text{H}_5\text{Br}$  in  $\text{CHCl}_3$  at  $25^\circ\text{ C}$ .

FIG. 5. The influence of pressure on the velocity of various reactions.

Table 6

The Influence of Pressure on the Reaction between Acetic Anhydride and Ethyl Alcohol in Toluene Solution at  $40^\circ\text{ C}$ . ( $\Delta V_c = -11.45$  c.c./gm. mole)

$P$ (atmospheres)	$k_p/k_0$	$k_p/k_0$
	Observed	Calculated
1	1.00	1.00
3,000	3.78	3.81
5,000	7.24	9.28
8,500	44.8	44.1

† Loc. cit.

Table 7

*Critical Increments of Volume for Reactions in Solution and in the Liquid Phase*

Reactants	Solvent	$t^{\circ}$ C.	$\Delta V_c$ (c.c./gm. mole)
<i>Cyclopentadiene</i>	Liquid	0	-18.6
		20	-20.8
		30	-23.1
		40	-26.1
$C_6H_5N + C_6H_5I$	$(CH_3)_2CO$	30.3	-16.4
		40	-17.6
		50	-18.6
		60	-19.6
$(CH_3CO)_2O + C_6H_5OH$	$C_2H_5OH$	20	-16.4
		30	-15.9
		40	-12.7
$(CH_3CO)_2O + C_6H_5OH$	$C_6H_5CH_3$	20	-9.6
		40	-11.4
		60	-12.5
		80	-12.9
$CH_3COOCH_3 + H_3O^+$	$H_2O$	14	-8.7
$CH_2ClCOO^- + OH^-$	$H_2O$	40	-6.1
		80.3	-6.2
$C_6H_5I + C_6H_5O^-$	$C_2H_5OH$	14.9	-3.7
		25.1	-4.1
$C_{12}H_{22}O_{11} + H_3O^+$	$H_2O$	15.5	+2.5
$(CH_3)(C_6H_5)(C_6H_5)(C_6H_5CH_3)NBr$	$CHCl_3$	25.0	+3.3
		35.0	+3.3
		44.9	+3.9

critical increments of volume calculated from the results of Newitt and Wassermann† on the rate of association of liquid *cyclopentadiene*.

Before discussing these results, we shall take a further step in reducing the volume of material to manageable proportions by interpolating or extrapolating, wherever possible, the term  $\Delta V_c$  to the common temperature of 25° C. The results (Table 8) help us to get the facts into their perspective.

The slowest of these reactions, in the sense used in this book, is the one most influenced by pressure: at 2,000 atmospheres its rate is 6 times as fast as at 1 atmosphere. The next two reactions, which are also slow reactions, though not so slow, have rates increased nearly fourfold by the same increase in pressure. Little can

† *Trans. Chem. Soc.*, 735, (1940).

be derived from the data on the ionic reaction, which is known to consist of quite a number of concurrent changes. Moreover, pressure probably affects the rate indirectly by adjusting the equilibrium

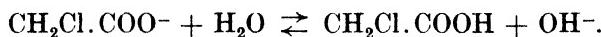


Table 8

*The Influence of Pressure on the Bimolecular Velocity Coefficient of Reactions in Solution at 298.1° K.*

Reaction	Solvent	$\Delta V_c$ (298.1° K.) (c.c./gm. mole)	$\left( \frac{k_{2000 \text{ atm.}}}{k_{1 \text{ atm.}}} \right)_{298.1^\circ}$
Dimerization of cyclopentadiene	Liquid	-21.8	5.98
$\text{C}_5\text{H}_5\text{N} + \text{C}_2\text{H}_5\text{I}$	$(\text{CH}_3)_2\text{CO}$	-15.8	3.64
$(\text{CH}_3\text{CO})_2\text{O} + \text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_5\text{OH}$	-16.1	3.73
$\text{CH}_2\text{Cl} \cdot \text{COO}^- + \text{OH}^-$	$\text{H}_2\text{O}$	-10.2	2.30
$\text{C}_2\text{H}_5\text{I} + \text{C}_2\text{H}_5\text{O}^-$	$\text{C}_2\text{H}_5\text{OH}$	-4.1	1.40

The reaction least affected by pressure is that one which is also most free from complications and in closest agreement with the predictions of the collision theory in its simplest form. In point of fact, the distinction between slow and normal reactions is less in the magnitudes of  $k_{2000}/k_1$ , than in the complete form of the pressure-velocity curve. Whereas, in the case of slow reactions, pressure seems to have a continuously favourable effect, in the ease of the normal reaction, the influence of very high pressures seems to reach a limit, as if no pressure, however great, could cause more than a fourfold increase. On the whole, the results of Table 8 show relatively small differences of pressure effects upon reactions which, based on other criteria, are members of very different groups. No kinetic classification of reactions in solution could have been justified from observations on the effects of pressure alone.

Gibson, Fawcett, and Perrin,† who found the following constants for the Hecht reaction in ethylalcoholic solution:

$$\text{at 1 atmosphere: } k_2 = 2.13 \times 10^{11} \times e^{-20740/RT};$$

$$\text{at 2,980 atmospheres: } k_2 = 3.72 \times 10^{11} \times e^{-20800/RT},$$

have concluded that, up to the pressure measured, the effect of increasing the pressure is almost entirely reflected in an increase of the collision number (see also Table 9).

† *Loc. cit.*

Table 9

*Arrhenius Constants,  $A_P$ ,  $E_P$  and  $A_V$ ,  $E_V$  for the Dimerization of Liquid Cyclopentadiene*

$P$ (atmo- spheres)	$E_P$	$\frac{RT^2\alpha}{\beta} \left( \frac{d \ln k}{dP} \right)_T$	$E_V$	$\log_{10} A_P$	$\log_{10} A_V$
		(Kilocalories/gm. mole)			
1	$16.6 \pm 0.4$	4.1	$20.7 \pm 0.7$	$6.1 \pm 0.3$	$9.2 \pm 0.5$
1,000	$17.7 \pm 0.4$	1.4	$19.1 \pm 0.8$	$7.4 \pm 0.3$	$8.1 \pm 0.5$
3,000	$18.6 \pm 0.4$	1.1	$19.7 \pm 0.7$	$8.8 \pm 0.3$	$8.8 \pm 0.5$

*The Relation between the Activation Energies measured at Constant Pressure and at Constant Volume*

The general form of the Arrhenius equation has now been accepted in the differential notation,

$$E_A = RT^2 \frac{d \ln k}{dT}, \quad (14)$$

rather than in the integrated form which Arrhenius himself used, and it has been assumed that the energy increment so calculated is that which holds at constant pressure. For greater precision, we may define the apparent energies of activation at constant volume and at constant pressure, respectively, by the formally similar differential equations

$$E_V = RT^2 \left( \frac{d \ln k}{dT} \right)_V \quad (15)$$

and  $E_P = RT^2 \left( \frac{d \ln k}{dT} \right)_P. \quad (16)$

It is a matter of some interest to find the relation between  $E_V$  and  $E_P$  for reactions in solution, but the task is, unfortunately, beyond computation at present. An approximate form, valid for pure liquid systems, can, however, be given, and as almost all reactions in solution can be measured at great dilutions, the appropriate equation for the pure solvent should lie near to that for the actual solution.

If it were known in advance what were the number and nature of the independent variables in terms of which the velocity coefficient could be expressed, the problem would be a straightforward one. It is, however, one of the major tasks of chemical kinetics to discover such parameters. The simplest assumption that can be made is that two variables suffice to determine the velocity constant of reactions

in the liquid state. The obvious choice is the pressure,  $P$ , and the temperature,  $T$ . Then let

$$\ln k = f(P, T). \quad (17)$$

Any change whatsoever in  $k$  may then be represented as the sum of two terms, viz.

$$d \ln k = \left( \frac{d \ln k}{dP} \right)_T dP + \left( \frac{d \ln k}{dT} \right)_P dT. \quad (18)$$

We are, of course, equally justified in assuming that the velocity coefficient is a function of the volume,  $V$ , and the temperature. Then let

$$\ln k = f(V, T), \quad (19)$$

so that

$$d \ln k = \left( \frac{d \ln k}{dV} \right)_T dV + \left( \frac{d \ln k}{dT} \right)_V dT. \quad (20)$$

As equations (18) and (20) are equally valid for any change in  $k$ , we may eliminate  $d \ln k$  from them, obtaining, after rearrangement,

$$\left( \frac{d \ln k}{dT} \right)_V = \left( \frac{d \ln k}{dT} \right)_P - \left( \frac{dV}{dT} \right)_P \left( \frac{dP}{dV} \right)_T \left( \frac{d \ln k}{dP} \right)_T.$$

Reference to equations (15) and (16) then enables us to write

$$E_V = E_P - RT^2 \left( \frac{dV}{dT} \right)_P \left( \frac{dP}{dV} \right)_T \left( \frac{d \ln k}{dP} \right)_T \quad (21)$$

as the relation between the apparent energies of activation. But the coefficients of isobaric expansion and isothermal compression are defined by the well-known relations

$$\alpha = \frac{1}{V} \left( \frac{dV}{dT} \right)_P \quad (22)$$

and

$$\beta = -\frac{1}{V} \left( \frac{dV}{dP} \right)_T. \quad (23)$$

Hence

$$E_V = E_P + \frac{RT^2 \alpha}{\beta} \left( \frac{d \ln k}{dP} \right)_T. \quad (24)$$

This equation† has been applied by Newitt and Wassermann‡ to the kinetics of the dimerization of cyclopentadiene in the liquid phase, with results which are shown in Table 9. The authors conclude 'that, in contrast to  $E_P$  and  $A_P$ , which increase markedly with increasing pressure, the pressure dependence of the activation energies  $E_V$  and

† Evans and Polanyi, *loc. cit.*

‡ *Trans. Chem. Soc.*, 735, (1940).

of  $A_V$  is smaller than the experimental error. It follows, therefore, that

$$E_P \text{ (pure liquid state)} - E_V \text{ (gas)}$$

and  $A_P \text{ (pure liquid state)}/A_V \text{ (gas)}$

are functions of the pressure, whereas

$$E_V \text{ (pure liquid state)} - E_V \text{ (gas)}$$

and  $A_V \text{ (pure liquid state)}/A_V \text{ (gas)}$

are independent of the pressure within the limits of the experimental error and the range referred to.<sup>1</sup> Their belief that the parameters of the equation

$$k = A_V e^{-E_V/RT} \quad (25)$$

are 'more characteristic of kinetics in the condensed state' than those of equation

$$k = A_P e^{-E_P/RT} \quad (26)$$

is well founded.

#### *A Discussion on the Difference between $E_P$ and $E_V$*

The Arrhenius constant,  $E_A$ , the apparent energy of activation as ordinarily measured, refers to the energy increment at constant pressure, and is in this section designated  $E_P$ . If  $E_P$  in general turns out to be very different from  $E_V$ , the energy increment at constant volume, much of the ground will be taken from beneath our feet, as previous developments have largely assumed the difference to be small. We shall therefore estimate the difference for certain pure solvents, and accept the results as giving correctly the order of magnitude of the difference which is likely to hold for reactions measured in them. For this purpose alternative forms of relation (24) may first be derived.

By combining it with equation (12) we see that

$$E_V - E_P = -\frac{T\alpha\Delta V_c}{\beta}. \quad (27)$$

A glance at Table 7 shows that  $\Delta V_c$  is generally negative, so that, as a rule,  $E_V$  is greater than  $E_P$ . The distinction between them vanishes at the absolute zero of temperature. We next observe that, since the kinetic pressure exerted by molecules in a fluid can be expressed as

$$\pi = \frac{T\alpha}{\beta}, \quad (28)$$

the difference between the two energies of activation becomes

$$E_V - E_P = -\pi\Delta V_c. \quad (29)$$

Finally, making use of the well-known relation between the two specific heats and the molar volume,  $V_m$ , which is

$$C_P - C_V = \frac{\alpha^2 V_m T}{\beta}, \quad (30)$$

it follows that  $\dot{E}_V - E_P = -\frac{(C_P - C_V)}{\alpha} \frac{\Delta V_c}{V_m}$ . (31)

The molecular volumes of many liquids have the order of magnitude of 100 c.c., which, in conjunction with the experimental findings summed up in Table 7, enable us to estimate the fraction  $-\Delta V_c/V_m$  as about 1/10. Because  $C_P - C_V$  is much greater for non-polar than for polar liquids,† it might at first be thought that the difference between  $E_V$  and  $E_P$  would be greater when they are used as solvents. It happens, however, that the coefficient of cubical expansion is also much greater for non-polar than for polar liquids, so that the two effects largely cancel each other, and we can, on general grounds, expect both classes of solvents to exert comparable influences on the energy of activation.

Let us consider in greater detail the magnitude of the correction in the case of acetone as a solvent. The coefficients of cubical expansion, evaluated from the densities,‡ are shown in the second column of Table 10. The compressibilities, listed in column 4, have been computed from the relative volumes measured by Bridgman§ at 20° and 80° C., under great pressures. Using values of  $\Delta V_c$  calculated from the influence of pressure on the velocity of reaction, we obtain an approximately constant value of about 2,000 calories for  $E_V - E_P$  in the case of the reaction between pyridine and ethyl iodide in acetone solution (Table 10). The apparent energies of activation of the reactions



in acetone solution were found (Table V (4)) to have an average value of 18,895 calories, when R ranges from  $\text{C}_3\text{H}_7$  to  $\text{C}_{16}\text{H}_{33}$ . Assuming  $E_V - E_P$  to have the same value, the corrected energies of activation have an average value of 21,020 calories. The correction gives us a value of  $A_V$  which is nearer the calculated collision frequency, Z, than was the uncorrected term  $A_P$ .

The difference,  $E_V - E_P$ , in water is smaller, and may even be of

† Schulze, *Phyeikal. Z.*, **26**, 153, (1925); Moelwyn-Hughes, *Physical Chemistry*, p. 316, Cambridge, (1940).

‡ *International Critical Tables*, vol. iii.

§ *Loc. cit.*

Table 10

*An Estimate of the Difference between  $E_P$  and  $E_V$  for the Reaction between Pyridine and Ethyl Iodide in Acetone Solution*

$T$ ( $^{\circ}$ K.)	$\alpha \times 10^3$ (degree $^{-1}$ )	$\Delta V_e$ (c.c./gm. mole)	$\beta \times 10^{10}$ (cm. $^2$ /dyne)	$E_V - E_P$ (calories/grm. mole)
303·1	1·5085	-16·4	0·990	1,809
313·1	1·5315	-17·6	1·035	1,944
323·1	1·5545	-18·6	1·080	2,066
333·1	1·5775	-19·6	1·125	2,188

opposite sign. At 15° C., for example, it can be shown from the data of Table 7, using known values of the coefficients of expansion and compression, that  $E_V - E_P$  for the hydrolysis of methyl acetate is +207 calories, and for the hydrolysis of sucrose is -59 calories. These are small corrections, but it is not their magnitude which is important; the variation of the correction with temperature may be considerable, though data are not at present available to test the point. The corrections bring both slow and fast reactions nearer to the normal category. It can also be shown that, unless the pressure effect is about ten times as great for hydrolyses in general as it is for the reactions considered here, the present correction can only partly account for the observed departures from the integrated equation of Arrhenius.

#### *The Variation of the Activation Energy with Respect to Pressure*

By applying the van 't Hoff isochore,

$$\Delta H = RT^2 \left( \frac{d \ln K}{dT} \right)_P \quad \text{VI (23)}$$

to equation (5), we obtain the following relation between the increase  $\Delta H_P$ , in heat content at a pressure,  $P$ , and that at zero pressure:

$$\Delta H_P = \Delta H_0 + P \Delta V^0 \left\{ 1 - \left( \frac{d \ln \Delta V^0}{d \ln T} \right)_P \right\}. \quad \text{(32)}$$

Using van 't Hoff's argument, which forms the basis of the treatment given in this chapter, we find the kindred relationship† between the energies of activation:

$$E_P = E_0 + P \Delta V_c \left\{ 1 - \left( \frac{d \ln \Delta V_c}{d \ln T} \right)_P \right\}. \quad \text{(33)}$$

† In the original derivation (Moelwyn-Hughes, *Trans. Faraday Soc.*, **32**, 1724, (1936)), an additional term appeared (last term in equation 55 of that paper) which should not have been there. The error has been very fully discussed by Evans and Polanyi (*ibid.*, **33**, 449, (1937)) and by Guggenheim (*ibid.*, **33**, 607, (1937)).

When the pressure effect follows Moesveld's rule (equation (13)), it is seen that

$$E_P = E_0 + P\Delta V_c. \quad (34)$$

The energy of activation, measured at a constant pressure, should thus vary linearly with respect to the pressure. Some values calculated from it are given in Table 11. With such small variations in the energy it is at present impossible to assess the range of validity of the theoretical treatment. Better agreement is obtained by using

*Table 11*

*The Variation of the Energy of Activation (calories/gram mole) with respect to Pressure*

Reaction	Solvent	Pressure (atmo- spheres)	<i>E<sub>P</sub></i>	
			Observed	Calculated
$\text{C}_2\text{H}_5\text{O}^- + \text{C}_2\text{H}_5\text{I}$ $(\Delta V_c = -3.9 \text{ c.c.})$ $E_0 = 20,740)$	$\text{C}_2\text{H}_5\text{OH}$	3,000	20,800	20,670
		5,000	20,340	20,620
$\text{CH}_3\text{ClCOO}^- + \text{OH}^-$ $(\Delta V_c = -6.15 \text{ c.c.})$ $E_0 = 22,730)$	$\text{H}_2\text{O}$	2,980	22,440	22,660
		7,600	21,330	22,550
		12,000	20,710	22,450
$(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_3)\text{NBr}$ $(\Delta V_c = +3.5 \text{ c.c.})$ $E_0 = 29,660)$	$\text{CHCl}_3$	3,000	29,200	29,730

the less restricted equation (33). The term  $\{1 - (d \ln \Delta V_c / d \ln T)_P\}$  may have positive values, as in the Menschutkin reaction in acetone, where it is about +2.8, or negative values, as in the case of the reaction between acetic anhydride and ethyl alcohol in ethylalcoholic solution, where it is -0.66. The pressure effect on the velocity of bimolecular reactions in solution must thus be listed among other effects which are specific for the reaction and the solvent medium.

## XII

### REACTIONS IN HETEROGENEOUS SYSTEMS INVOLVING SOLUTIONS

WHEN a chemical reaction occurs in a heterogeneous system, there are superimposed on to the specific chemical effects certain interfacial factors which operate at the boundary of the phases and may influence the velocity of chemical change. A large variety of phenomena thus becomes possible theoretically, and is in fact found. Even within the circumscription of the title of this chapter are included vaporization, crystallization, dissolution of gases and solids, and chemical reaction, both catalysed and uncatalysed. Most of the experimental work, however, has been restricted to solid-liquid systems, consisting of a solid in contact with a dilute solution, and it is with this rather diversified category of chemical change, which forms the logical prelude to enzyme reactions, that we shall begin.

Dissolved molecules may react with a solid, present as a crystal or dispersed as a colloid, or may undergo catalytic transformation at its surface. Since the dissolved molecules must strike the surface of the solid before reaction can occur, the change takes on the nature of a bimolecular process, with the possibility of intermediate complexes of varying natures and stability. Solute molecules may anchor on the solid surface with the tenacity of a chemical link, or they may merely congregate in greater number about the surface than in the bulk of the solution, and be held loosely there by attractive forces not necessarily chemical in origin. In both cases the molecules are said to be adsorbed on the surface. Since the approach of an ion or a solute molecule up to the surface, or its removal therefrom, entails the expenditure of energy, the observed critical increment of a heterogeneous reaction is usually a composite term, consisting of the true energy of activation plus the heat of adsorption or desorption as the case may be. Surface reactions may thus be examined in the light of the intermediate-complex theory, but the heat of formation of the complex acquires a slightly different meaning. In addition to adsorption, three distinct processes occur in reactions of this kind: (1) solute molecules approach and collide with the solid surface, where (2) chemical reaction takes place; followed by (3) recession of the products from the interface into the bulk of the solution. Each of these three

processes may influence the net rate of reaction, the magnitude of which is determined by the slowest process of all. Diffusion always plays a part in process (3), and sometimes in process (1).

Two of the complications with which we have to contend, therefore, are the diffusion and the adsorption of solutes. Due to the influence of Nernst and of Langmuir, the kinetics of reactions in heterogeneous systems have been usually presented in terms of either of these phenomena. In the first edition of this work, however, we showed that there are quite a number of carefully investigated reactions in heterogeneous systems which can adequately be interpreted without appealing to the concept of diffusion or adsorption; several further instances could now be added. On account of their simplicity, and the harmony necessary in a general development of the subject, we shall deal with them first.

### *The Reaction between Solid Calcium Carbonate and Dilute Hydrochloric Acid*

When a crystal of marble dissolves in hydrochloric acid, the rate of evolution of carbon dioxide is found to be proportional to the area,  $S$ , of the surface of the solid and to the concentration of the acid. Equimolecular solutions of strong acids have all the same effect.

$$+\frac{d[\text{CO}_2]}{dt} = kS[\text{H}^+]. \quad (1)$$

Spring† worked with parallelepipeds of Carrara marble, waxed all over but for one facet, which was exposed to a 5 per cent. solution of hydrochloric acid. The facet measured 19 mm. by 16 mm. and at 35° C. gave off carbon dioxide at the rate of 25 c.c. in 54 seconds. This is equal to  $1.14 \times 10^{18}$  molecules per second. From the temperature coefficient of this rate, it is found that  $E_{15-35^\circ} = 6,300$  calories and  $E_{35-55^\circ} = 6,400$  calories. Over a temperature range of 40°, therefore, there is a constant  $E_A$  of about 6,350 calories.‡ The calculated rate of disappearance of hydrogen ions is

$$-\frac{dn_s}{dt} = Sn_s \sqrt{\left(\frac{RT}{2\pi M_s}\right)} e^{-E/RT}. \quad \text{I (18)}$$

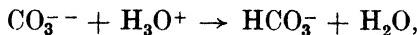
$S$ , the area of the solid, is here equal to 3.04 sq. cm., and

$$n_s \sqrt{\frac{RT}{2\pi M}},$$

† *Z. physikal. Chem.*, **1**, 209, (1887).

‡ A repetition of Spring's work by King and Lin (*J. Amer. Chem. Soc.*, **55**, 1928, (1933)) gives  $E_A = 5,820 \pm 770$  calories.

the number of hydrogen ions which strike unit surface per second, is here equal to  $5.08 \times 10^{24}$ . If the chemical change consists of the removal of carbonate ions from the crystal



the subsequent decomposition of the soluble bicarbonate may be assumed rapid, so that one molecule of carbon dioxide is produced for each hydrogen ion which disappears as a result of collision with the surface. The result of these calculations is that about one ion out of every 42 which strike the surface with energy greater than  $E_A$  results in chemical change. This factor is quite a reasonable one. The important conclusion is that the necessity of postulating the existence of an interfacial layer is superfluous. Diffusion does not determine the velocity of reaction in this case. Brunner,<sup>†</sup> whose absolute rates are about 4 times as great as those of Spring—possibly due to the stirring<sup>‡</sup>—favours the diffusion view, but his study of the temperature effect is not extensive enough to warrant the conclusion.

*The Decomposition of Sodium Hypochlorite in Aqueous Solution, catalysed by Cobalt Peroxide*

Howell<sup>§</sup> has studied the velocity of decomposition of sodium hypochlorite ( $2\text{ClO}^- \rightarrow 2\text{Cl}^- + \text{O}_2$ ) under the influence of cobalt peroxide. A suspension of  $\text{CoO}_2$  containing 0.033 gram molecule per litre was found to be quite stable, and to give reproducible results when the rate of stirring exceeded 1,600 revolutions per minute. When the concentration of catalyst is low, the decomposition is unimolecular with respect to hypochlorite, the value of the unimolecular constant being directly proportional to the concentration of catalyst over a sixfold range in  $[\text{CoO}_2]$ . At 40° C., 1 c.c. of the catalyst preparation added to 60 c.c. of hypochlorite solution gives  $k_{\text{uni}} = 3.51 \times 10^{-3}$  (minutes<sup>-1</sup>:  $\ln_e$ ). Howell measured the velocity of reaction at temperatures of 25, 30, 35, 40, 45, and 50° C., and found  $E_A$  to be 16,574 calories.

The molecular statistics of this reaction may now be discussed, provided the size of the catalyst particles can be estimated. From the stability of the preparation it may safely be inferred that the

<sup>†</sup> *Ibid.*, **47**, 56, (1904).

<sup>‡</sup> It is not logical to apply to reactions carried out with violent stirring the diffusion coefficient which has been determined in quiet solutions. The diffusion of a solid in a stirred liquid is discussed by Schumann, *Physical Rev.*, **37**, 1508, (1931).

<sup>§</sup> *Proc. Roy. Soc., A*, **104**, 134, (1923).

diameters are less than  $10^{-6}$  cm., for particles of this size coagulate rapidly. Ascribing a value of  $5 \times 10^{-7}$  cm. to the diameter of the cobalt peroxide suspensoid, and assuming it to have unit density, it follows that under the experimental conditions (1 c.c. of 0.033 molar preparation added to 60 c.c. of hypochlorite solution) 1 c.c. of the reaction mixture contains  $7.52 \times 10^{14}$  particles of catalyst. The observed unimolecular constant is  $5.85 \times 10^{-5}$  seconds<sup>-1</sup>. The unimolecular constant which would be observed when the concentration of catalyst is 1 particle per c.c. is thus  $7.78 \times 10^{-20}$  seconds<sup>-1</sup>.

Let us now calculate the velocity upon the assumption that each ion  $\text{ClO}^-$  which strikes the catalyst with energy greater than 16,574 calories/gram molecule brings about the formation of one molecule of oxygen. The number of molecules striking unit area per second is  $n_s \sqrt{(RT/2\pi M_s)}$ , where  $n_s$  is the number of hypochlorite ions per c.c. and  $M_s$  is the ionic weight. The number which strikes a sphere of area  $\pi\sigma^2$  is  $n_s \sigma^2 \sqrt{(\pi RT/2M_s)}$ . Taking  $\sigma$  to be  $5 \times 10^{-7}$  cm., and  $T = 313^\circ$ , this becomes  $7.05 \times 10^{-9} n_s$ . The fraction of this number with the requisite energy is  $e^{-16574/RT} = 2.46 \times 10^{-12}$ ; the number of activating collisions upon one particle per second is  $1.73 \times 10^{-20} n_s$ . Hence  $dn_s/dt = 1.73 \times 10^{-20} n_s$ , or  $k = 1.73 \times 10^{-20}$ , which is in excellent agreement with the observed velocity constant. The closeness of the agreement, however, is not important and may well be accidental. The result, nevertheless, is conclusive in demonstrating that the reaction velocity is governed by activated collisions with the surface and not by diffusion.

The general equation applicable to similar cases is

$$\frac{dn_s}{dt} = \sigma_c^2 n_s n_c \sqrt{\left(\frac{\pi RT}{2M_c}\right)} e^{-E/RT}, \quad (2)$$

where  $n_s$  and  $n_c$  are the numbers of substrate and catalyst units present per c.c., and  $\sigma_c$  is the diameter of the catalyst. It will be noticed that the collision term in this equation is the same as that derived for gaseous molecules,

$$Z_B = \sigma_{1,2}^2 n_1 n_2 \sqrt{\left(8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right)}, \quad I(21)$$

under such extreme conditions as will allow us to ignore  $1/M_2$  as negligibly small, and to take the sum of the molecular radii as equal to the radius of the larger molecule.

Howell found that the addition of sodium chloride accelerated the

reaction, the velocity constant being linearly related to the amount of added salt, thus affording an interesting example of the linear salt effect in heterogeneous catalysis. The catalyst suffers no injury when the usual poisons—potassium cyanide, mercuric chloride, arsenious oxide, and hydrogen sulphide—are added. Alkalies, however, retard the reaction markedly, possibly, as Howell suggests, due to selective adsorption.

Chirnoaga's repetition of this work† gives results which agree in the main with those of Howell, although  $E$  is found to be somewhat less (15,840). With nickel peroxide as catalyst  $E$  becomes 16,580 calories, but the reaction is no longer unimolecular, the rate being given approximately as  $dc/dt = kc^{0.47}$ . The difference is rather surprising in view of the similarity in the two catalysts and in the apparent heats of activation.

Other examples of heterogeneous reactions, the rates of which are not governed by diffusion, are the oxidation of hydrocarbons by potassium permanganate,‡ the hydrolysis of emulsions of esters in water,§ the dissolution of arsenious oxide,|| and the interaction of solid copper with sulphur ( $S_s$ ) in carbon tetrachloride solution, for which  $E_A$  is zero.††

Kinetic principles have also been profitably applied to a variety of heterogeneous problems in which a solid surface and a solution are concerned. These include the standard electrode potential,††† the ageing of the surfaces of solutions,†††† the velocity of crystallization,††††† and overpotential.†††††

### *The Kinetics of Coagulation*

We have drawn a sharp distinction between the collision frequencies of molecules possessing the large kinetic energies usually necessary for chemical reaction, and those of molecules which collide while still possessing only the equipartition energy (Chapter VIII)

† *Trans. Chem. Soc.*, 1693, (1925).

‡ Meyer and Saam, *Berichte*, **30**, 1935, (1897).

§ Goldschmidt, *Z. physikal. Chem.*, **31**, 235, (1899).

|| Drucker, *ibid.*, **36**, 693, (1901).

†† R. S. Bradley, *Trans. Faraday Soc.*, **34**, 278 (1938).

††† J. A. V. Butler, *ibid.*, **19**, 729, (1924).

†††† K. S. G. Doss, *Proc. Indian Acad. Sci.*, **4**, 97, (1936).

††††† Birstein and Blumenthal, *Bull. de l'Acad. Polonaise des Sciences et des Lettres*, p. 399, Cracovie, (1937).

††††† De Béthune and Kimball, *J. Chem. Physics*, **13**, 53, (1945).

Smoluchowski's expression for the frequency of binary collisions in the latter case is

$${}_A Z_B = \frac{kT}{3\eta} n_A n_B \frac{(r_A + r_B)^2}{r_A r_B}. \quad \text{VIII (4)}$$

If nothing further is necessary for physicochemical change, the rate of disappearance of either *A* or *B* molecules is given by this equation. The bimolecular velocity coefficient when the colliding particles are identical is then clearly

$$k_2 = \frac{4kT}{3\eta}. \quad (3)$$

The coagulation of colloid particles takes place at every binary encounter, as Zsigmondy† has shown by comparing the rate of coagulation of gold sol in water with the value afforded by this expression. A still more extensive verification is provided by the experiments of Wiegner and Tuorila‡ on the same system. Some of their results, with fine and coarse gold sols at room temperatures, are summarized in Table I. Bimolecular coagulation coefficients calculated from them by means of the relation

$$k_2 = 1/n_0 t_{1/2} \quad \text{II (15)}$$

are also included. We note, in the first place, that  $k_2$  has a value of  $6.84 \times 10^{-12}$  c.c. per particle-second, which is constant to within

*Table 1*

*The Coagulation Coefficients of Colloidal Particles in Aqueous Solution*

Colloid	<i>r</i> (Å.)	$n_0$ (number of particles per c.c. at the start)	$t_{1/2}$ (time of half- completion, in seconds)	$k_2 \times 10^{12}$ (c.c./particle- second)
Gold	970	$3.6 \times 10^8$	507	5.48
	—	$6.2 \times 10^8$	254	6.35
	320	$1.06 \times 10^9$	134	7.04
	512	$2.02 \times 10^9$	79	6.27
	53.7	$5.80 \times 10^{11}$	0.208	8.29
	36.9	$8.44 \times 10^{11}$	0.186	6.36
	29.1	$2.93 \times 10^{12}$	0.0424	8.05
	29.1	$4.87 \times 10^{12}$	0.0275	7.47
	36.9	$5.91 \times 10^{12}$	0.0269	6.29
Kaolin	3,040	$8.9 \times 10^8$	211	5.33

20 per cent., though the initial concentrations have been varied by a factor of 17,000. The slight variations are irregular, and do not generally exceed differences observable in a given run, which often

† *Z. physikal. Chem.*, **92**, 600, (1918).

‡ *Kolloid-Zeitschrift*, **38**, 3, (1926).

amount to  $\pm 15$  per cent. of the average. Even if genuine, they indicate a dilution effect which is much smaller than has hitherto been found for bimolecular changes in the gaseous phase or in solution. We note, in the second place, an excellent agreement with the predicted value of Smoluchowski's theory. At 20° C., the viscosity of water is  $1.005 \times 10^{-2}$ ; hence the calculated value of  $k_2$  is  $5.33 \times 10^{-12}$  c.c. per particle-second. The observed coagulation coefficient for a coarse kaolin dispersion, which happens to be identical with this theoretical value, has been included merely to illustrate the fact that  $k_2$  is not chemically specific.

The viscosity of air at 20° C. is 55 times less than the viscosity of water.  $k_2$  for the coagulation of aerosols should therefore exceed that for collosols by this factor, and be about  $2.93 \times 10^{-10}$  c.c. per particle-second. The experimental values† vary from  $8 \times 10^{-10}$  for smokes formed from metallic oxides, such as MgO and CdO, to  $5 \times 10^{-10}$  for smokes formed from resin and fatty acids. Agreement between experiment and theory is thus not quite so good in gaseous systems as in solution, and several hypotheses have been advanced to explain the discrepancy factor of from 1.7 to 2.7.‡ Among them are the statistical distribution of particle size, investigated by Smoluchowski, and the vaporization from the particulate surface and the inadequacy of Stokes's law, investigated by Whytlaw-Gray and his collaborators. If we are prepared to allow these various influences jointly to account for a factor of about 2, we may conclude that the simple diffusion theory is adequate to explain the absolute rate of coagulation of all colloid particles, in solution and in the gaseous phase, irrespective of their radii and chemical composition. The temperature coefficient, moreover, is correct.§

The problem may also be regarded from the more conventional angle of chemical kinetics as a bimolecular process with zero energy of activation between particles which increase in size as the reaction proceeds. For normal bimolecular reactions with zero energy of activation,  $k_2$  is, as we have seen (p. 70), usually about  $4.8 \times 10^{-10}$  cm.<sup>3</sup> sec.<sup>-1</sup>. Its approximate constancy is due to the fact that the slowness of motion of the massive molecules is almost exactly offset by the larger target area which they offer for collisions. Clearly the simple

† Whytlaw-Gray, *Trans. Chem. Soc.*, 268, (1935).

‡ Whytlaw-Gray and Patterson, *Smoke*, Arnold, (1932).

§ P. J. R. Butler, *Trans. Faraday Soc.*, 34, 656, (1930).

collision theory is capable of explaining the bimolecular nature of the coagulation process and the order of magnitude of the bimolecular velocity coefficient. The assumptions necessary for its application are that each particle in the cloud moves with the equipartition value which it would have if it were a single molecule, and that encounters between two particles are a sufficient condition for coagulation. The treatment may be artificially simplified by regarding the cloud as homogeneous throughout its history, i.e. by imagining the decrease in the molecular population caused by the coalition of two particles to be evenly shared between all the particles. Let

$a$  = the radius at time  $t$ , of the particles, assumed to be all of equal size,

$a_0$  = the initial radius of the particles,

$k$  = Boltzmann's constant,

$m$  = mass of one molecule of the dispersoid,

$\mu$  = mass of one particle in the smoke,

$M$  = total mass of dispersed compound in 1 cm.<sup>3</sup>

$n_L$  = number of molecules per cm.<sup>3</sup> of liquid or solid forming the particles,

$N$  = number of particles per cm.<sup>3</sup> at time  $t$ ,

$N_0$  = number of particles per cm.<sup>3</sup> initially,

$t$  = time, in seconds, and

$T$  = absolute temperature.

Then the rate of decrease in the concentration of particles is

$$-\frac{dN}{dt} = 16 \left( \frac{\pi k T}{\mu} \right)^{\frac{1}{2}} a^2 N^2. \quad (4)$$

The constancy of the mass concentration may be expressed as follows:

$$M = N \mu = \frac{4}{3} \pi a^3 N n_L m. \quad (5)$$

Eliminating  $\mu^{\frac{1}{2}}$  and  $a^2$  we obtain

$$-\frac{dN}{dt} = K N^{11/6}, \quad (6)$$

where

$$K = 8 \left( \frac{3kT a_0}{n_L m} \right)^{\frac{1}{2}} N_0^{\frac{1}{6}}. \quad (7)$$

Integration of equation (6) leads to

$$K = \frac{6}{5t} (N^{-\frac{1}{6}} - N_0^{-\frac{1}{6}}). \quad (8)$$

Coagulation should thus not be an exact bimolecular process, though it may well be experimentally indistinguishable from one. The velocity coefficient,  $K$ , though constant for a given system, increases in proportion to  $M^{\frac{1}{2}}$ . The experimental value of  $k_2$ , obtained from the formula  $-dN/dt = k_2 N^2$ , is then approximately

$$k_2 \doteq 8 \left( \frac{3kT a_0}{n_L m} \right)^{\frac{1}{2}}. \quad (9)$$

Thus for particles of unit density ( $n_L m = 1$ ) coagulating at 20° C. with  $k_2 = 5 \times 10^{-10}$ , we should expect the initial radii to be  $3.24 \times 10^{-8}$  cm. Coagulation therefore starts off with single molecules.

### *The Diffusion of Solutes*

When there is an unequal concentration of solute, and the solution is consequently not at equilibrium, there is a resultant osmotic force driving the molecules from the region of high concentration to that of low concentration, and tending to establish equilibrium by bringing about the most random distribution of solute molecules. The ions or dissolved molecules under these conditions are said to diffuse through the solution. Since an adsorbed layer of molecules is formed at the surface of any solid in contact with a solution, the process of diffusion tends to uniform such a layer.

Fick† found that the number,  $dN$ , of molecules of solute which cross a boundary of area  $S$  in time  $dt$  is proportional to the concentration gradient  $dn/dz$ :

$$dN = -DS \frac{dn}{dz} dt. \quad (10)$$

The proportionality factor is termed the diffusion coefficient, and is seen to have the dimensions of (length)<sup>2</sup>/time. It can be determined experimentally by analysing layers at various heights in a tall cylinder which originally contained a concentrated layer of the solute in contact with a large volume of the solvent.

The kinetic theory of diffusion has been given by Einstein.‡ A cylinder of unit cross-section containing a dilute solution is imagined to be fitted with a semi-permeable membrane, through which only solvent molecules can pass. If the concentration of the solute in compartment  $A$  is greater than in  $B$ , a force  $F$  will be exerted on the piston, which is equal to the difference in osmotic pressure. Now the osmotic pressure  $p$  is related to the concentration  $n$  by the van 't

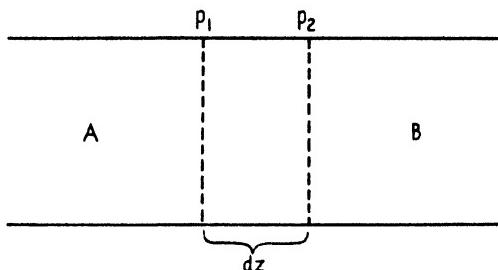
† *Pogg. Annalen*, 94, 59, (1855).

‡ *Z. Elektrochem.*, 14, 235, (1908).

Hoff laws  $p = nkT$ , provided the solution is moderately dilute. Hence the difference in the osmotic pressures is  $dp = kT dn$ , and this equals the net directional force. The number of molecules in the compartment is  $ndz$ . The net force exerted by one molecule is consequently

$$F = -\frac{kT}{n} \frac{dn}{dz}.$$

The negative sign appears because the force acts in a direction opposed to the direction of increasing concentrations. By Stokes's



law, the resistance offered to the motion of each spherical molecule is  $6\pi\eta r$ ; hence the uniform velocity of diffusion should be

$$v = -\frac{kT}{n} \frac{dn}{dz} \frac{1}{6\pi\eta r}.$$

But  $-vn/(dn/dz)$  represents the number of molecules transported per second across unit area under unit concentration gradient, and is therefore simply the diffusion coefficient. Hence

$$D = \frac{kT}{6\pi\eta r}. \quad (11)$$

This is the familiar Stokes-Einstein diffusion equation.

The relation between the velocities of ions under unit concentration gradient and their velocities under unit electrical potential was deduced by Nernst.<sup>†</sup> Assuming a uni-univalent electrolyte to be completely ionized in dilute solution, the diffusion coefficient is related as follows to the absolute velocities ( $u_a$  and  $u_c$ ) of the ions in an electrostatic field of unit potential gradient:

$$D = 2RT \left( \frac{u_a u_c}{u_a + u_c} \right). \quad (12)$$

Numerical values of the coefficient of diffusion obtained by Öholm<sup>‡</sup>

<sup>†</sup> *Z. physikal. Chem.*, **2**, 613, (1888).

<sup>‡</sup> *Ibid.*, **50**, 309, (1905).

and by Haskell† show that  $D$  is in fact inversely proportional to the radius of the solute, as estimated by equation I(17), though it leads to a smaller value of  $r$ . Thus, for example, in water at 18° C., urea, hydroquinone, and sucrose have values of  $1 \cdot 12 \times 10^{-5}$ ,  $0 \cdot 73 \times 10^{-5}$ , and  $0 \cdot 41 \times 10^{-5}$  sq. cm. per second respectively. According to equation (11), the energy of diffusion is

$$E_D = RT^2 \left( \frac{d \ln D}{dT} \right)_P = RT - RT^2 \left( \frac{d \ln \eta}{dT} \right)_P = RT + B. \quad (13)$$

As far as experiments allow of a decision, this relation also is obeyed, even for solvents showing variable values of  $B$ . The data of Orr and J. A. V. Butler‡ on the diffusion of deuterium hydroxide (DOH) in water, which may almost certainly be taken as equal to the self-diffusion of water, are reproduced in Table 2. By equating the

*Table 2  
The Diffusion of Deuterium Hydroxide in Water*

$T$ (°K.)	$D \times 10^6$ (cm. <sup>2</sup> sec. <sup>-1</sup> )	$\eta \times 10^8$ (gm. cm. <sup>-1</sup> sec. <sup>-1</sup> )	$(D\eta/T) \times 10^{10}$
273.2	1.46	17.86	9.5
287.4	1.94	11.65	7.9
298.1	2.64	8.949	7.9
308.1	3.88	7.208	9.1
318.1	4.75	5.970	8.9
Average			$8.7 \pm 0.8$

average experimental value of  $D\eta/T$  to the theoretical equivalent  $k/6\pi r$ , we find  $r$  to have the value  $0.84 \pm 0.07$  Å. Above 10° C., Orr and Butler find the simple exponential formula

$$D_{\text{DOH in HOH}} = 0.197 \times e^{-5300/RT}$$

to reproduce the facts to within their experimental certainty. The average value of  $RT + B$  within this temperature region is known with some accuracy to be 4,400 calories.

#### *Nernst's Theory of the Kinetics of Heterogeneous Reactions*

By rotating cylinders of benzoic acid and of lead chloride in water, and analysing the solution from time to time, Noyes and Whitney§ found that the velocity of dissolution of the solids followed an apparently unimolecular law

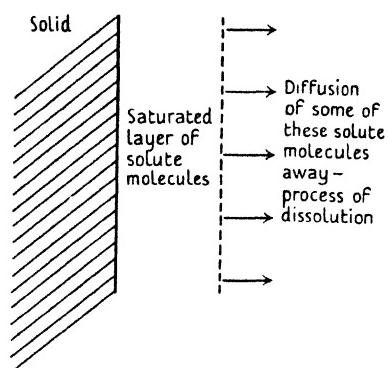
$$\frac{dn}{dt} = k_1(n^0 - n). \quad (14)$$

† *Physical Review*, 27, 145, (1908).

‡ *Z. physikal. Chem.*, 23, 689, (1897).

§ *Trans. Chem. Soc.*, 1273, (1935).

$n^0$  is the solubility of the solid in water, and  $n$  the concentration of the solute in the bulk of the solution at time  $t$ . The rate of dissolution being proportional to the difference between the saturated and observed concentrations, it was suggested by them that a saturated



layer is formed at the surface of the solid. The velocity of the change is then simply the velocity with which solute molecules diffuse out into the liquid. Bruner and St. Tolloczkó† found the rate of dissolution of a variety of compounds in water to be directly proportional to the area ( $S$ ) of the surface:

$$\frac{dn}{dt} = k'_1 S(n^0 - n). \quad (15)$$

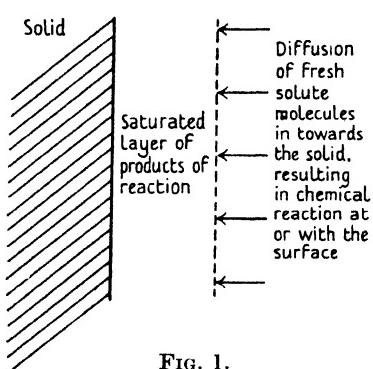


FIG. 1.

Since unimolecularity is obeyed during the complete process, it appears that the effective area remains constant, although the actual surface of the solid becomes eroded.

A general theory of the kinetics of heterogeneous reactions was developed by Nernst‡ upon analogy with the effects observed during dissolution.

The principal postulate is that chemical reaction proper takes place

very rapidly at the surface, the liquid in the immediate neighbourhood thus becoming soon choked with the products of reaction and hindering further chemical change. Fresh molecules of solute can, however, diffuse slowly through this saturated layer, with a velocity which is small compared with that of the chemical change, and diminishes as the concentration of dissolved substance falls off. The theory therefore predicts that such reactions must be unimolecular, with a velocity which is equal to the velocity of diffusion. Nernst's theory has been variously received. Brunner§ in particular adopted it as a comprehensive answer to the phenomena of all chemical

† *Z. physikal. Chem.*, 35, 283, (1900).

‡ *Ibid.*, 47, 52, (1904).

§ *Ibid.*, 47, 58, (1904).

reactions occurring between solids and dilute solutions. Wildermann,<sup>†</sup> inclined to discredit the theory altogether, pointed out, quite rightly, that the unimolecular behaviour can be explained in other ways. Experiments carried out during later years, a review of which is given by Centnerszwer,<sup>‡</sup> show that some reactions can readily be understood upon the Nernst theory, whereas others seem to contradict it. The crux of the matter depends on the assumption that chemical reaction or dissolution takes place rapidly compared with diffusion, and this, we now know, is not always true.

The theory of Nernst may be described in the following words. Consider a solution of volume  $V$  c.c., containing  $n$  molecules of solute per c.c. Between the solution and a solid of area  $S$  sq. cm.,

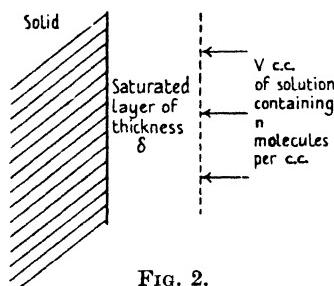


FIG. 2.

there is a layer of thickness  $\delta$ , formed by the accumulation of reaction products during initial stages. In the subsequent stages, fresh molecules of solute can only reach the solid by diffusion through this layer. The number of molecules reaching the solid in time  $dt$  seconds is  $dN$ . The fall in concentration in this time is  $dN/V$ . Now by Fick's law

$$\frac{dN}{dt} = -DS \frac{dn}{dz}, \quad (10)$$

where  $dn/dz$  is the concentration gradient. Hence

$$\frac{dn}{dt} = \frac{1}{V} \frac{dN}{dt} = -\frac{DS}{V} \frac{dn}{dz}.$$

Nernst assumes that the concentration gradient at any instant is given by the term  $n/\delta$ , which, as Drucker<sup>§</sup> has pointed out, is by no means a satisfactory expression. The exact one, however, is difficult to obtain. On this basis, we have

$$-\frac{dn}{dt} = \frac{DS}{V\delta} n, \quad (16)$$

and the observed unimolecular constant is thus

$$k_1 = DS/V\delta. \quad (17)$$

From the experimental value of  $k_1$  corresponding to unit area of solid

<sup>†</sup> *Ibid.*, **66**, 445, (1909).

<sup>‡</sup> *Ibid.*, **A**, **141**, 297, (1929).

<sup>§</sup> *Loc. cit.*

and unit volume of solution, the somewhat fictitious thickness,  $\delta$ , may be found, for then  $\delta = D/k_1$ . For a number of reactions in water at 20° C.,  $\delta$  is about  $3 \times 10^{-3}$  cm. This is a physically improbable result, but the fact that it is roughly the same for many reactions of a wholly different chemical nature is consistent with the view that the rates are determined by the process of diffusion. This is the really significant result.

A more important test of Nernst's theory is afforded by the influence of temperature upon the velocity of heterogeneous reactions. Provided the thickness of the interfacial layer is independent of temperature,  $dk_1/dT$  should equal  $dD/dT$ , and the observed critical increment should thus be about 4,500 calories at 25° C. Many heterogeneous reactions do in fact have about this value for  $E_A$ , but it is quite possible, of course, for reactions to possess a real energy of activation of this value. Homogeneous reactions in solution are known with zero critical increment.

A third characteristic of reactions with rates governed by the diffusion process is that  $k$  varies with the rate at which the solution is stirred. The constant  $s$  in the equation: rate of reaction = constant  $\times$  (rate of stirring) $^s$  has been given values of 1 (Wildermann),  $\frac{2}{3}$  (Brunner), and  $\frac{1}{2}$  (von Name).

Two instances may be discussed by way of illustration.

#### *The Reactions between Metals and Iodine dissolved in Aqueous Potassium Iodide*

The velocity of the reaction between metals and iodine has been studied by von Name and his collaborators.<sup>†</sup> The significant results are that numerous metals, such as mercury, cadmium, zinc, copper, and silver react at approximately the same velocity at the same temperature. The velocity increases with a rise in temperature to the same extent as the diffusion coefficient. Furthermore, bromine attacks the metals more rapidly than iodine. All these facts are adequately explained in terms of diffusion.

Von Name's<sup>‡</sup> data on the rate of reaction between cadmium and iodine are very complete. A disk of cadmium of diameter 3.83 cm. (area therefore equals 23.0 sq. cm.) was rotated 200 times per minute

<sup>†</sup> von Name and Edgar, *J. Amer. Chem. Soc.*, **38**, 253, (1916); von Name and Bosworth, *Am. J. Sci.*, **32**, 207, (1911); von Name and Hill, *ibid.*, **36**, 543, (1913).

<sup>‡</sup> *Ibid.*, **43**, 453, (1917); see also L. L. Bircumshaw and Everdell, *Trans. Chem. Soc.*, 598, (1942).

in a solution containing 0.5 gram molecules of potassium iodide per litre, 0.01 of sulphuric acid, and 0.02 of iodine. The halogen was therefore present almost entirely in the form of the tri-iodide ion  $I_3^-$ . The reaction was found to be unimolecular; the value being that given by the equation.

$$k = \frac{2.303}{t_2 - t_1} V \log_{10} \frac{[I_2]_1}{[I_2]_2} \quad (18)$$

$t$  is the time in minutes, and  $V$  the volume of the solution in c.c. Von Name's values are:

$t^\circ$ C.	0	15	25	35	45	55	65
$k$	3.72	5.87	7.62	9.55	11.81	14.26	16.93

The critical increment (4,040 calories) thus compares favourably with the energy of diffusion (equation (13)), which, although not constant, has an average value of 4,240 calories over this range. By equation (17) the thickness  $\delta$  of the saturated layer is again about  $10^{-3}$  cm. The same order of magnitude is found in the dissolution of glasses.<sup>†</sup>

### *The Reaction between Metals and Dilute Aqueous Acids*

The factors governing the rate of evolution of hydrogen from metals in acid solution have received much attention, partly on account of the importance attaching to the allied phenomena of metallic corrosion and passivity. A wide diversity of results has been discovered. It may be said that the general reproducibility of data obtained within recent years is singularly good. The velocity of reaction most frequently is unimolecular with respect to the acid, although changes of higher order have been reported. Many metals and some alloys are attacked by acids at approximately the same rate, indicating, along with other results, the predominance of the part played by diffusion.

A polished disk of metal, partially covered by a mixture of wax and rubber, is rotated in the solution of acid. The course of the reaction may be determined by weighing the disk at various intervals, or, as is more frequently done, by measuring the volume of hydrogen evolved. The velocity of the reaction between zinc and hydrochloric acid has been investigated using both methods. Some of the results are compared in Table 3.

<sup>†</sup> R. Müller, *Acta Physicochim. U.S.S.R.*, 4, 99, 481, (1936).

Table 3

*The Rate of Reaction between Zinc and Hydrochloric Acid referred to 1 sq. cm. of Metal Surface*

Refer- ence	Tempera- ture °C.	Initial concen- tration of HCl (gm. mol./litre)	Observed no. of $H_3O^+$ disappearing per second	Calculated no. of $H_3O^+$ striking unit area per second	Ratio
(1)	23	0.175	$3.10 \times 10^{17}$	$1.52 \times 10^{23}$	$4.9 \times 10^6$
(2)	16	0.5	$1.36 \times 10^{18}$	$4.20 \times 10^{24}$	$3.2 \times 10^6$
(3)	25	0.5	$1.08 \times 10^{18}$	$4.36 \times 10^{24}$	$4.0 \times 10^6$

(1) King and Braverman, *J. Amer. Chem. Soc.*, **54**, 1744, (1932).

(2) Fischer, *Z. Elektrochem.*, **35**, 502, (1929).

(3) Centnerszwer, *Z. physikal. Chem.*, **A**, **141**, 297, (1929).

The figures in the fourth column have been computed from the number of c.c. of hydrogen evolved per minute: those in column 5 have been obtained from the expression  $n_s\sqrt{(RT/2\pi M)}$ , where  $n_s$  is the number of hydrogen ions per c.c. of solution (equation I (18)). As in the reaction between metals and iodine, only a very small fraction of those ions which reach the surface result in chemical change. In the present example, two hydrogen ions must become engaged before one atom of zinc is dissolved, which suggests that the low efficiency of the reaction may be attributed to the smaller probability of what is in effect a ternary collision. This explanation, however, is improbable, for the same tardiness is revealed in the process of dissolution of a salt in water. The origin of the delay at the surface seems to be due to the necessity of activation of the solid molecules. In the most favourable case, the minimum value of the energy of activation would be equal to the heat of fusion of the solid plus the heat of solvation. When  $E$  is large, the reaction at the surface will be slow, and possibly much slower than diffusion, which does not therefore enter into the scheme. In the instance under examination, however, the actual chemical change at the surface, although relatively slow, is still much faster than the rate of diffusion. Hence nothing is known of the true energy of activation. King and Braverman† have shown this reaction to be free from kinetic salt effects and due entirely to hydrogen ions.‡ From their values of  $k_{25}/k_{18}$  ( $= 1.285$ ), and  $k_{35}/k_{25}$  ( $= 1.260$ ), we have an apparent energy of activation of

† *Loc. cit.*

‡ The proportionality between velocity of dissolution and concentration of acid is disputed by Guertler and Blumenthal (*Z. physikal. Chem.*, **A**, **152**, 197, (1931)), who emphasize the role played by the overvoltage of hydrogen.

4,230 calories, which again is not very different from the heat of diffusion. Further confirmation that the measurable velocity is influenced by diffusion is afforded by the effect of stirring and of the addition of substances which alter the viscosity.

The alloying of zinc with small amounts of silver, lead, arsenic, and other metals diminishes the velocity of reaction to a slight extent.† The rate of reaction frequently increases during the initial stages before the unimolecular condition is established. Calculations directed at evaluating the thickness of the Noyes-Whitney layer on the assumption that the early period in the reaction corresponds with the time taken to form the layer show the assumption to be false. The rate of dissolution of metals in acids is modified by the application of an external electromotive force, the magnitude of the modification being proportional to the applied E.M.F.‡

Centnerszwer§ claims that the reactions between cadmium and hydrochloric acid and between tin and hydrochloric acid are of the fourth order with respect to the acid, but the evidence adduced is not convincing. The absolute rate is slower by a factor of about  $10^3$  than the rate with zinc and other metals, and is certainly a function of  $[HCl]$  raised to a power greater than unity. Centnerszwer's results on tin in hydrochloric acid give a value of  $E_A = 7,210$  calories, from which it is found that the ratio of the number of activating collisions to the number of molecules reacting is about  $10^5$ .

Experiments on the dissolution of metals|| and amalgams†† in non-aqueous solutions of acids are few in number, and indicate a solvent effect.

#### *An approximate Theory of Heterogeneous Reactions governed by Diffusion*

It is worth while attempting to find how far heterogeneous reactions may be capable of interpretation in terms of the diffusion theory, without appealing to the physically unsatisfactory concept of a diffusion layer, some 50,000 molecules thick. Only an approximate solution is possible.

We start with Fick's law for the rate of increase in concentration

$$\frac{dn}{dt} = -\frac{DS}{V} \frac{dn}{dz} \quad (19)$$

† Fischer, *loc. cit.*      ‡ Thiel and Eckell, *Z. physikal. Chem.*, **132**, 78, (1928).

§ *Ibid.*, **A**, **141**, 297, (1929).      || Zecchini, *Gazz. chim. ital.*, **27**, 466, (1897).

†† Brönsted and Kane, *J. Amer. Chem. Soc.*, **53**, 3624, (1931).

and with the more general expression of the diffusion theory

$$\frac{dn}{dt} = D \frac{d^2n}{dz^2}. \quad (20)$$

At the stationary state, which is always assumed to be rapidly attained,  $dn/dt$  is zero at all distances from the surface, and, since  $D$  is itself not zero, it follows that

$$\frac{d^2n}{dz^2} = 0, \quad (21)$$

the general solution of which is

$$n = a + bz. \quad (22)$$

The constants  $a$  and  $b$  are to be determined by the boundary conditions. We may take

$$n = n^0 \quad \text{when } z = 0 \quad (23)$$

$$\text{and} \quad n = \bar{n} \quad \text{when } z = V/2S. \quad (24)$$

$$\text{Hence} \quad n = n^0 + \frac{2S}{V} (\bar{n} - n^0)z. \quad (25)$$

$n^0$  is the saturation concentration and  $\bar{n}$  the average concentration. It follows that

$$-\frac{dn}{dt} = D \left( \frac{S}{V} \right)^2 (n^0 - n) \quad (26)$$

so that the unimolecular velocity coefficient,  $k_1$ , reckoned on the saturation deficiency, is simply

$$k_1 = D \left( \frac{S}{V} \right)^2. \quad (27)$$

This result seems satisfactory numerically, as far as one can obtain data for quiescent systems.

A more elaborate attempt along similar lines has been made by Roller.<sup>†</sup>

### *The Kinetics of Dissolution*

Gases, like solids, dissolve in liquids with a velocity that is proportional to the difference between the actual and the saturated concentration of solute.<sup>‡</sup> It is with the latter, upon which almost all the work has been done, that we shall deal here, using Berthoud's method<sup>§</sup> for synthesizing the spontaneous-escape and the diffusion mechanisms.

<sup>†</sup> *J. Physical Chem.*, **39**, 221, (1935).

<sup>‡</sup> Becker and Pearson, *Sci. Proc. Roy. Dublin Soc.*, **17**, 197, (1923).

<sup>§</sup> *J. Chim. Phys.*, **10**, 633, (1912).

The dissolution of a solid into a liquid resembles in many respects the escape of molecules from the surface of a liquid or solid into a gaseous atmosphere. In both systems the velocity may be determined by a diffusion mechanism or by what may be termed a spontaneous-escape mechanism. Let

$S$  = the surface area of the solid ( $\text{cm.}^2$ ),

$n_s$  = number of molecules per unit area of the surface of the solid,

$n$  = the concentration (molecules/c.c.) of solute in the bulk of the solution,

$n'$  = the concentration of solute molecules in the diffusion layer,

$n^0$  = the saturation concentration of solute molecules,

$\delta$  = the thickness of the diffusion layer (cm.).

The rate of dissolution we shall denote by  $\bar{v}n_s S$ . The rate of deposition of solute molecules on to the solid is assumed to be proportional to the surface area,  $S$ , and to concentration of solute molecules in solution. The number of molecules dissolving per second is thus

$$+\frac{dN}{dt} = \bar{v}n_s S - k_s n S. \quad (28)$$

When the solution is saturated,  $dN/dt$  is zero, and therefore

$$\bar{v}n_s = k_s n^0. \quad (29)$$

Eliminating  $\bar{v}n_s$  from equations (28) and (29), we have (since  $N = nV$ )

$$+\frac{dn}{dt} = \frac{k_s S}{V} (n^0 - n). \quad (30)$$

This equation implies that the number of molecules dissolving in unit time is proportional to the area and to the difference between the actual and the saturation concentrations. Reckoning the time from the instant when the solid starts to dissolve in the pure solvent, the integrated form of equation (30) becomes

$$k = \frac{V}{St} \ln \frac{n^0}{n^0 - n_t}$$

or

$$n_t = n^0(1 - e^{-k_s St/V}), \quad (31)$$

where  $n_t$  is the concentration of dissolved molecules at time  $t$ .

If the rate of dissolution is governed by diffusion of solute molecules through a layer of thickness  $\delta$ , the concentration at the solid surface, denoted by  $n'$ , is less than the saturated concentration. According to

Fick's law, the number of molecules diffusing through this layer in unit time, across an area  $S \text{ cm.}^2$ , is

$$+\frac{dN}{dt} = -DS\frac{dn}{dx}. \quad (19)$$

But  $n = N/V$ , and  $dn/dx = (n - n')/\delta$ ; therefore

$$+\frac{dn}{dt} = \frac{DS}{V\delta}(n' - n). \quad (32)$$

Assuming  $D$  to be independent of  $n$ , we have, on integration,

$$\frac{D}{\delta} = \frac{V}{St} \ln \frac{n'}{n' - n}$$

or

$$n = n'(1 - e^{-DSl/V\delta}). \quad (33)$$

Reverting to the general equation (30), we see that, when  $n'$  is the molecular concentration in the diffusion layer, the rate of dissolution is  $(kS/V)(n^0 - n')$ . Combining with equation (32) we have

$$+\frac{dn}{dt} = \frac{k_s S}{V}(n^0 - n') = \frac{DS}{V\delta}(n' - n). \quad (34)$$

Hence

$$n' = n^0 \frac{k_s + (n/n^0)(D/\delta)}{k_s + (D/\delta)}. \quad (35)$$

When the rate of spontaneous dissolution is relatively rapid ( $k \gg D/\delta$ ),  $n' \rightarrow n^0$ , i.e. the concentration of molecules in the diffusion layer approaches the saturation value, and the net rate of dissolution is governed by the diffusion process. When the rate of spontaneous dissolution is relatively slow ( $k \ll D/\delta$ ),  $n' \rightarrow n$ , i.e. the diffusion layer does not exist. Eliminating  $n'$  from equations (34) and (35), we obtain

$$+\frac{dn}{dt} = \frac{k_s S(n^0 - n)}{V\{1 + (k_s \delta/D)\}}$$

or

$$n_t = n^0 \{1 - e^{-(k_s S/V)(1 + (k_s \delta/D))t}\}. \quad (36)$$

This equation of Berthoud reduces to that of Noyes and Whitney (equation (31)) when  $k_s \ll D/\delta$ , and to that of Nernst (equation (33)) when  $k_s \gg D/\delta$ .

Diffusion determines the rate when  $\delta \gg D/k_s$ , and spontaneous dissolution when  $\delta \ll D/k_s$ . Now  $D$  does not vary much for a variety of solids in water, or for a variety of vapours in air at atmospheric pressure, hence the choice of mechanism is determined largely by the magnitude of  $k_s$ . This, in turn, according to equation (29) is  $\bar{v}n_s/n^0$ .

Unless  $\bar{v}$  is a highly specific frequency, therefore, a diffusion mechanism is to be expected for the dissolution of relatively insoluble solutes, and for the vaporization of relatively involatile liquids.

The application of these kinetic principles to the determination of solubilities is obvious; and one example must suffice. The increase in heat content attending the dissolution of benzoic acid in water is  $5,780 \pm 910$  calories,† and the critical increment for the dissolution is  $5,630 \pm 570$  calories.‡ The postulated equilibrium condition is given by equation (29). On substituting  $(kT/2\pi m)^{\frac{1}{2}}$  for  $k_s$  and

$$(kT/h)\exp(-E/RT)$$

for  $\bar{v}$ , following Herzfeld (Appendix 1), the theoretical expression for the equilibrium concentration (i.e. the solubility) of the solute becomes

$$n^0 = \frac{(2\pi mkT)^{\frac{1}{2}} n_s}{h} e^{-E/RT}. \quad (37)$$

As a rough estimate, we may take  $1/n_s$ , which is the average area of a molecule on the crystal surface to be  $50 \times 10^{-16}$  cm.<sup>2</sup>; we then find, at 25°,  $n^0 = 1.42 \times 10^{19}$  molecules per c.c., which compares well with the experimental value of  $1.44 \times 10^{19}$ , or 0.343 grams per 100 c.c. Coherence with the rates of dissolution can then readily be shown to bring down the value of  $\delta$  to sub-molecular dimensions ( $\sim 10^{-9}$  cm.).

### *The Kinetics of Reactions at the Air-Liquid Interface*

Thanks to Langmuir, Rideal, and Adam, our knowledge of the properties of matter in the interfacial phase has been vastly extended during recent years.§ In this work we must restrict ourselves to the kinetics of reactions between solute molecules and molecules in an interfacial layer. The latter can, with a suitable choice of molecular structure, substrate concentration, and temperature, be made to stand almost as we want them. Both the trough technique of Langmuir and Adam and the interfacial-potential technique of Schulman and Rideal are powerful implements, enabling the investigator almost to touch the molecules which are reacting.

When we consider all the kinetic information available on the

† Bourgoin, *Ann. Chim. Phys.*, **15**, 171, (1878).

‡ Wildermann, *Z. physikal. Chem.*, **66**, 445, (1909).

§ Langmuir, *J. Amer. Chem. Soc.*, **38**, 2221, (1916); Rideal, *Surface Chemistry*, 2nd ed., Cambridge, (1930); Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., Oxford, (1941); see also J. K. Roberts, *Some Problems in Adsorption*, Cambridge, (1939), and S. Brunauer, *The Adsorption of Gases and Vapours*, Oxford, (1943).

reaction of dissolved molecules with molecules in the interface, the first impression conveyed is one of striking similarity with the corresponding information on the kinetics of the bimolecular processes when both reactants are in solution. This remark applies to a variety of chemical changes, which includes the saponification of esters,<sup>†</sup> the oxidation of fatty acids,<sup>‡</sup> the digestion of proteins,<sup>§</sup> the polymerization of unsaturated compounds,<sup>||</sup> and extends even to points of detail. Thus, for example, the rates of reaction of the halogens with substituted phenols in a film are, like their rates in bulk solution, governed by collisions of the organic molecule with the hypohalous acid HOX or the trihalide ion  $X_3^-$ , rather than by collisions with the halogen molecule,  $X_2$ . Moreover, the relative reactivities stand in the order HOI > HOBr > HOCl and  $I_3^- < Br_3^- < Cl_3^-$  in both phases.<sup>††</sup> When a given reaction is compared in the two systems, however, we observe most interesting points of dissimilarity, which have done much to settle the question of the so-called orientation factor, and to contribute to our estimate of the role of electrostatic influences.<sup>‡‡</sup>

Experiment shows that the number of molecules reacting per second is proportional to the area,  $S$ , of the interface, to the surface concentration,  $n_s$ , of one reactant and to the bulk concentration,  $n$ , of the other:

$$-\frac{dN}{dt} = k_2 S n_s n. \quad (38)$$

In order to have measurable rates of change, it is necessary to ensure that there are many more molecules of solute in solution than there are of molecules in the film. During chemical change, therefore, the bulk concentration of the soluble reactant remains sensibly constant. The total number of molecules in the film is  $N = S n_s$ , so that

$$-\frac{dn_s}{dt} = k_2 n n_s. \quad (39)$$

Because  $n$  remains virtually unchanged, we have

$$k_1 = -\frac{1}{n_s} \frac{dn_s}{dt} = k_2 n, \quad (40)$$

<sup>†</sup> Fosbinder and Rideal, *Proc. Roy. Soc., A*, **143**, 61, (1933).

<sup>‡</sup> A. H. Hughes and Rideal, *ibid.*, **140**, 253, (1933).

<sup>§</sup> Schulman and Rideal, *Biochem. J.*, **27**, 1591, (1933).

<sup>||</sup> Gee and Rideal, *Trans. Faraday Soc.*, **31**, 969, (1935).

<sup>††</sup> Alexander, *Trans. Chem. Soc.*, **729**, (1938).

<sup>‡‡</sup> Rideal, *Liversidge Lecture of the Chemical Society, Trans. Chem. Soc.*, **423**, (1945).

a proportionality which has been generally established. At constant surface pressure,  $k_1$  is derived from the measurement of the area,  $A$ , per molecule:

$$A = A_0 e^{-k_1 t} + A_\infty (1 - e^{-k_1 t}). \quad (41)$$

If the product of reaction is soluble,  $A_\infty$  is clearly zero, so that

$$A = A_0 e^{-k_1 t}. \quad (42)$$

For measurements carried out at constant molecular area,  $k_1$  is obtained from the analogous expression for the temporal variation of the interfacial potential.<sup>†</sup>

The kinetics of reactions between interfacial and dissolved molecules closely resemble bimolecular behaviour in solution when the film is of the expanded type.  $k_2$  for ethyl palmitate reacting with sodium hydroxide at 20°, when the surface pressure is 3 dynes per cm., is  $5.87 \times 10^{-4}$  litres/gm. mole-second. The value for the reaction in solution is not, of course, known for this insoluble ester: if it could be measured, it would probably not exceed double this value (see Table V (4)). At the same surface pressure, the apparent energy of activation is 12,000 calories, again in good agreement with the figure for the saponification reaction in solution.<sup>‡</sup> It follows that the ratio,  $P$ , of the observed velocity to the calculated one is nearly the same in the two systems. In the case of the saponification of stearolactone, for example, Fosbinder and Rideal<sup>§</sup> calculate a value of  $8.2 \times 10^{-5}$  using the collision formula which is proportional to  $T^{\frac{1}{2}}$ , and 0.21 using the viscosity correction.

On compression, however, the apparent energy of activation rises, and the efficiency of activating collisions with the interface approaches unity (see Table 4, after Alexander and Rideal). The extrapolated

*Table 4*  
*The Interaction of Trilaurin with Aqueous Sodium Hydroxide at 20° C.*

$F$ (dynes/cm.)	$A \times 10^{16}$ (cm. <sup>2</sup> /molecule)	$k_1 \times 10^3$ (litres/gm. mol.-sec.)	$E_A$ (kilocal./gm. mole)	$P$
5.4	93.6	3.73	10.0	$1.1 \times 10^{-6}$
10.8	83.2	3.94	13.2	$3.1 \times 10^{-6}$
16.2	76.7	3.36	16.1	$4.1 \times 10^{-6}$

<sup>†</sup> Alexander and Rideal, *Proc. Roy. Soc., A*, **163**, 70, (1937).  $\xi = 4\pi n_s \mu$ , where  $\mu$  is the vertical component of the dipole (Adam, *ibid.*, **138**, 430, (1932); Adam and Harding, *ibid.*, **143**, 104, (1933)).

<sup>‡</sup> Alexander and Rideal, *loc. cit.*

<sup>§</sup> *Loc. cit.*

value of  $E_A$  corresponding to unit value of  $P$  is 17.8, in good agreement with the corrected value ( $E_A + B$ ) for saponifications in the bulk phase.

Part of the increase in  $E_A$  is doubtless due to the stronger electrostatic field exerted by the dipoles in the more condensed film. Taking  $D$  as 7, which is consistent with surface potential measurements, Alexander and Rideal estimate the maximum electrostatic contribution,  $E_e$ , due to the interaction of the approaching anion with the field exerted by a planar array of dipoles, to be only 2,800 calories, so that some other influence, such as the submersion of the short alkyl group on compression,† must also be at work.

The film reactions so far investigated afford no evidence that the rate is governed by diffusion of products away from the interface, or of new reactants through a layer of products. The values of  $\delta$  obtained by applying the Nernst theory is of the order of magnitude of  $10^{-9}$  cm., the thickness of the Helmholtz layer, beneath which the solute concentration may be regarded as equal to that in the body of the solution.

#### *A Comparison of the Catalytic Effects of a Plane Surface, an Inorganic Colloid, and an Enzyme*

Berzelius saw in the catalytic similarity of platinum and organic 'ferments' a way of studying enzyme action, which was soon followed by Bredig and his collaborators. More recent work has in fact shown that the similarity, if not amounting to identity, is much closer than the earlier workers imagined. This we shall illustrate with reference to the decomposition of hydrogen peroxide, a change which is almost invariably unimolecular.

(a) *Decomposition in the Absence of Catalyst.* The decomposition of aqueous solutions in glass vessels is partly heterogeneous, and is affected by the surface of the vessel and by dust particles suspended in the solution.‡ In quartz vessels, the change is apparently homogeneous.§ The velocity is also very susceptible to traces of hydroxyl and ferric ions.|| Using great precautions to purify the peroxide and to ensure a reproducible surface, fairly constant velocities of decomposition have been found by J. Williams†† and by Pana,‡‡ some of whose results are given in Table 5. Approximately 1-molar solutions were

† Alexander and Schulman, *Proc. Roy. Soc., A*, **161**, 115, (1937).

‡ F. O. Rice, *J. Amer. Chem. Soc.*, **48**, 2099, (1926); *J. Physical Chem.*, **31**, 1507, (1927). § A. C. Robertson, *J. Amer. Chem. Soc.*, **53**, 382, (1931).

|| Clayton, *Trans. Faraday Soc.*, **11**, 164, (1915).

†† *Ibid.*, **24**, 245, (1928).

‡‡ *Ibid.*, **24**, 486, (1928).

employed, so that the unimolecular velocity coefficient in waxed vessels at 25° C. takes on the value of  $3.45 \times 10^{-9}$  seconds<sup>-1</sup>, and the efficiency of activated solute-solvent collisions is about one in 10<sup>6</sup>.

Table 5

Surface of vessel	Initial rate of decomposition at 40° C. (grams of H <sub>2</sub> O <sub>2</sub> per c.c. per minute $\times 10^7$ )	$E_A$ (Calories per gram molecule)
Silica	3.50	16,800
Glass	1.05	17,000
Paraffin wax	0.30	18,000

(b) *Decomposition catalysed by Colloidal Platinum.* Highly reproducible results were obtained by Bredig and von Berneck† in their important researches on the catalytic influence of stable platinum sol. One gram atom of the metal dissolved in many millions of litres of solution has a pronounced catalytic effect. Velocity measurements taken at 25, 45, 65, and 85° C. give a critical increment of 11,700 calories, corrected for the spontaneous (uncatalysed) decomposition of the peroxide, but not for the coagulation of the sol. At 25° C., with 1/38,000 gram atom of platinum per litre, and a concentration of 1/50 gram molecule of hydrogen peroxide per litre, the unimolecular constant is  $2.34 \times 10^{-4}$  (seconds<sup>-1</sup>, ln<sub>e</sub>).

In order to compare this figure with the theoretical value, it is first necessary to know the number of colloid particles present. Their average diameter is known to be about  $8.8 \times 10^{-6}$  cm.‡ Let us assume that each atom of platinum in the colloid is associated with three molecules of water, the density of the particles being about 10 grams/c.c. On this basis, the number of colloid particles in each c.c. is  $1.84 \times 10^9$ . The number of molecules of hydrogen peroxide destroyed per c.c. per second is

$$(1/50) \times (1/1000) \times 6.06 \times 10^{23} \times 2.34 \times 10^{-4} = 2.83 \times 10^{15}.$$

One colloid particle therefore brings about the decomposition of  $1.54 \times 10^6$  molecules of hydrogen peroxide per second. The number of H<sub>2</sub>O<sub>2</sub> molecules colliding per second against a sphere of diameter  $\sigma$  is  $Z = \sigma^2 n_s \sqrt{(\pi R T / 2M)}$ .

$$\sigma = 8.8 \times 10^{-6}, \quad n_s = 1.21 \times 10^{19}, \quad M = 34.$$

Hence  $Z = 3.17 \times 10^{13}$ .

† *Z. physikal. Chem.*, 31, 258, (1899).

‡ Lewis, *A System of Physical Chemistry*, vol. i, p. 333, (1923).

The fraction of this number—with energy equal to 11,700 calories is  $e^{-E/RT} = 2.46 \times 10^{-9}$ . The number of activating collisions per second per colloid particle is thus  $7.78 \times 10^4$ . Rather than conclude, as would probably be legitimate in the absence of adsorption, that each activating collision causes the destruction of 20 molecules of hydrogen peroxide—thus suggesting a chain reaction—it must simply be concluded that the theory of collisional activation leads to a value of the velocity which lies as close to the experimental one as the nature of the assumptions will allow.

This conclusion has received confirmation in the work of Syrkin and Vassiliev,<sup>†</sup> which shows that, weight for weight, the catalytic efficiency of platinum is the same, even when dispersed on silica gel. The whole surface thus seems to be active.

(c) *Decomposition catalysed by Catalase.* The results of Willstätter and Pollinger,<sup>‡</sup> of Zeile and Hellström,<sup>§</sup> and of Williams,<sup>||</sup> upon the enzymic decomposition of hydrogen peroxide have been analysed and interpreted by Haldane.<sup>††</sup> Zeile and Hellström have shown that horse-liver catalase is an iron-porphorin compound with a spectrum resembling that of alkaline haematin, and that the quantity of iron present can be estimated photometrically by converting the enzyme into pyridine-haemochromogen. Haldane makes the assumption that a molecule of catalase contains one atom of iron, and on this basis shows that at 0° C. and at the optimum pH (6.6) one molecule of catalyst destroys  $5.42 \times 10^4$  substrate molecules per second. Plant catalase is slightly more active. A comparison of this figure with the one calculated above shows that inorganic catalysts and enzymes behave very similarly. The following figures refer to a solution which is 1/100-molar with respect to hydrogen peroxide at 0° C.:

One platinum colloid destroys  $1.26 \times 10^5$  molecules of hydrogen peroxide per second.

One unit of liver catalase destroys  $0.54 \times 10^5$  molecules of hydrogen peroxide per second.

One unit of plant catalase destroys  $1.7 \times 10^5$  molecules of hydrogen peroxide per second.

If the enzyme molecules contain, like haemoglobin, four atoms of iron

<sup>†</sup> *Compt. rend. Acad. Sci. U.S.S.R.*, **1**, 513, (1935).

<sup>‡</sup> *Annalen*, **430**, 290, (1923).

<sup>§</sup> *Z. physiol. Chem.*, **192**, 171, (1930).

<sup>||</sup> *J. General Physiol.*, **11**, 209, (1928).

<sup>††</sup> *Proc. Roy. Soc., B*, **108**, 559, (1931).

per molecule, the reactivity is commensurably greater, but of the same order of magnitude.

A careful examination of these figures shows that the agreement is, to some extent, accidental. When hydrogen peroxide is decomposed by colloidal platinum, it appears from the foregoing calculations that every molecule of the peroxide which strikes the colloid with an energy equal to 11,700 calories is decomposed. The chemical efficiency of the activating colloid-substrate encounter is not less than unity, and all parts of the colloid surface seem to be equally effective catalytically. Now the energy of activation for the decomposition by liver catalase is about 5,500 calories (Williams), so that we should expect one molecule of catalase to be more efficient than a platinum sol unit by the factor  $e^{\Delta E/RT}$ , where  $\Delta E = 11700 - 5500$ . The value of the exponential is  $9.6 \times 10^4$ . By an independent line of argument, without reference to colloidal platinum, Haldane has estimated the efficiency factor to be about  $6.6 \times 10^4$ . Apparently, therefore, only one out of about 90,000 molecules of hydrogen peroxide which strike the catalase molecule with sufficient violence is decomposed. In the case of the hydrolysis of sucrose by saccharase the factor is about 7,000.† After allowing for the possible error in  $E$ , which may be considerable even at the optimum pH, there remains justifiable evidence for concluding that enzymes are in fact less efficient than inorganic catalysts. The principal reason is that only a small fraction of the enzyme surface is catalytically active. This constitutes a major distinction between enzymes and inorganic catalysts.

As Haldane and Moelwyn-Hughes have shown, there is nothing to differentiate the decomposition of a catalase-hydrogen peroxide reaction from any ordinary unimolecular reaction in a gas or a liquid, and nothing to differentiate the saccharase-sucrose reaction from an ordinary bimolecular reaction in either system.

A similar conclusion has been reached by Easson and Steadman‡ in their study of the hydrolysis of acetyl-choline by esterase.

(d) *Decomposition catalysed by Massive Platinized Platinum.* In most respects this reaction is typical of the changes the rates of which are governed by the process of diffusion,§ as we should expect, since the chemical change occurring at the surface must be extremely rapid

† Moelwyn-Hughes, *Ergebnisse der Enzymforschung*, **2**, 1, (1933).

‡ Proc. Roy. Soc., **B**, **121**, 142, (1936).

§ Bredig and Teletow, *Z. Elektrochem.*, **12**, 582, (1906).

if massive platinum is catalytically comparable with the colloidal metal. The catalyst is poisoned by hydrocyanic acid, mercuric chloride, and iodine. Chloroform and alcohols are without effect, while formic acid, hydrazine, and dilute nitric acid have a promoting action, and have been termed catalytic tonics. The poisoning, or negative catalytic, effect is best understood in terms of selective adsorption. Promoter action may well be independent of the surface of the platinum, and due to separate catalysis in the homogeneous phase. The injury by the poisons is not permanent, and the health of the catalyst can readily be restored.

### *Enzyme Reactions*

Enzymes are colloidal catalysts of high molecular weight, at the surface of which substrate molecules undergo chemical change.† The subject of enzyme chemistry, like that of adsorption, has its origin and most of its growth in chemical kinetics. In no other field has the power of kinetic principles been more forcefully felt. Chemical kinetics is, in truth, less a circumscription of a branch of knowledge or a means of codifying ascertained facts, than an experimental method for extending the bounds of knowledge by the acquisition of new facts.

Enzymes are usually purified by consecutive adsorption on, and elution from, active surfaces of adsorbents such as kieselguhr. Increase in purity is attended by increase in catalytic activity; and it is symptomatic of the success of the kinetic method that one hundred per cent. purity as indicated by this method should have coincided so closely with the absolute purity now attainable from crystalline enzymes, with well-defined molecular weights, and X-ray patterns. Table 6 gives Northrop's summary on the molecular weight of pepsin, obtained by a variety of methods.

With such precision at our command, there need be no hesitation in applying firm physicochemical methods to enzyme catalysis, which exhibit phenomena as reproducible as can be found in any other system. Let us, therefore, apply Langmuir's theory to enzyme catalysis.

Let the catalyst have  $n_0$  sites per cm.<sup>2</sup> of surface, on which a substrate molecule or ion can be adsorbed, and let  $\theta_s$  be the fraction

† Detailed references to work mentioned in this section will be found in *Ergebnisse der Enzymforschung*, 2, 1, (1933); *ibid.*, 6, 23, (1937); and *Handbuch der Enzymologie*, p. 220, Akademische Verlagsgesellschaft, Leipzig, (1940).

*Table 6*  
*The Molecular Weight of Pepsin*

Method	Molecular weight
Osmotic pressure	35,000
Coefficient of diffusion	36,000
Sedimentation velocity	35,500
Sedimentation equilibrium	39,200
Chemical analysis (1 atom of phosphorus per molecule)	39,800
" (2 atoms of chlorine)	35,000
" (10 atoms of sulphur)	36,000

of these sites which are occupied under equilibrium conditions. The number of molecules desorbed per second is  $S n_0 v_s \theta_s$ , and the number adsorbed per second is  $S k_s n_s (1 - \theta_s)$ . At equilibrium, these two rates are equal, so that

$$\theta_s = \frac{k_s n_s}{k_s n_s + v_s n_0}. \quad (43)$$

If the rate of reaction is governed by the number of adsorbed substrate molecules, the velocity of chemical change, for a given enzyme concentration, should be proportional to the substrate concentration,  $n_s$ , when  $n_s$  is low, and independent of it when  $n_s$  is high. This behaviour is, perhaps, the most characteristic feature of enzyme action, as we have seen from our derivation of the Michaelis law (equation I (41)) according to the stationary state hypothesis. Armstrong showed it to hold for the hydrolysis of lactose by emulsin, Hudson found it to apply to the hydrolysis of sucrose by saccharase, and Northrop proved it to be true for the digestion of casein by trypsin. The later work of Kuhn and Sobotka and of Weidenhagen makes it clear that there are few exceptions among thermal reactions. Genuine deviations are provided by oxidative systems for which the Michaelis constant is negative. These reactions are best understood in terms of the theory of branching chains, advanced in a qualitative way by Haber and Willstätter, and quantitatively formulated by Moelwyn-Hughes.

If there are  $n_E$  molecules of enzyme per c.c. of solution, the total surface in  $V$  c.c. of solution is clearly

$$S = n_E A V, \quad (44)$$

where  $A$  is the area of one molecule of enzyme. Then, since  $N = V n_s$ ,

$$-\frac{dn_s}{dt} = A n_E n_0 v_s \theta_s. \quad (45)$$

At every concentration of enzyme, therefore, the rate of reaction is proportional to it: this also is generally true.

Reference to equation (43) shows that the concentration,  $n'_s$ , which corresponds to one-half of the limiting velocity, is

$$n'_s = n_0 \frac{\nu_s}{k_s} = K_m. \quad (46)$$

Using Herzfeld's expression (Appendix I) for the average frequency of desorption,

$$\nu_s = (kT/h)e^{-E_1/kT}, \quad (47)$$

and Knudsen's expression for the frequency of adsorption,

$$k_s = (kT/2\pi m_s)^{1/2} e^{-E_2/kT}, \quad (48)$$

we see that the Michaelis constant is

$$K_m = \frac{(2\pi m_s kT)^{1/2} n_0}{h} e^{-E_1/kT} = \frac{(2\pi m_s kT)^{1/2}}{A' h} e^{-E_1/RT}, \quad (49)$$

where  $A'$  is the area of one site, and  $E = E_1 - E_2$ .

Euler's experimental value of  $K_m$  for the sucrose-saccharase system at 3° C. is  $1.22 \times 10^{22}$  molecules/c.c., and for  $E$  is 2,000 calories/gm.-mole. A comparison of these figures with the radius of the enzyme as determined from the coefficient of diffusion shows that the number of active centres on each enzyme is at least one, and may possibly be as many as 8.

If the fractional number of sites that is covered, at equilibrium, by a second solute of type  $I$  is  $\theta_I$ , then the fractional free surface is now  $(1 - \theta_s - \theta_I)$ . Since both  $dn_s/dt$  and  $dn_I/dt$  are zero in the stationary state, we have

$$\theta_s = \frac{k_s n_s}{k_s n_s + \nu_s n_0 + k_I n_I (\nu_s / \nu_I)}. \quad (50)$$

Had there been no second solute to adsorb, the fractional free surface would have been

$$\theta_s^0 = \frac{k_s n_s}{k_s n_s + \nu_s n_0}. \quad (51)$$

The relevant ratio is

$$\frac{\theta_s^0}{\theta_s} = 1 + \frac{k_I (\nu_s / \nu_I) n_I}{k_s n_s + \nu_s n_0}, \quad (52)$$

which, at high substrate concentration, reduces to

$$\frac{\theta_s^0}{\theta_s} = 1 + \left( \frac{k_I}{k_s} \right) \left( \frac{\nu_s}{\nu_I} \right) \frac{n_I}{n_s}. \quad (53)$$

Any solute which, while not reacting, is more strongly adsorbed than the reactant solute must act as an inhibitor, and the relative rates of

reaction in the absence and in the presence of inhibitor is proportional to  $n_f$ . Euler and Svanberg's results on the inhibition of the same reaction by mercuric chloride obeys this rule, and the energy of dissociation of the enzyme-inhibitor complex can be shown to exceed that of the enzyme-substrate complex by 6,500 calories.

In order to examine the molecular statistics of an enzyme action, we must be assured, first, that the rate is not one that is governed by diffusion, and, second, that during catalytic change there is no appreciable inactivation of the enzyme. Such conditions are met with in the hydrolysis of sucrose by saccharase. It is desirable to learn how this reaction, judged solely upon experimental facts, compares with simple bimolecular processes. During the initial stages the reaction is unimolecular with respect to the sugar, and its velocity is directly proportional to the concentration of enzyme employed. The value of the constant at 37° C. and pH 4.5 is  $2.1 \times 10^{-4}$  seconds<sup>-1</sup>, when the solution contains 0.06 gram of crude saccharase per 100 c.c. By a somewhat indirect method it can be shown that this represents a concentration of pure saccharase not exceeding  $5 \times 10^{-9}$  gram molecule per litre. The bimolecular constant is thus at least  $4.2 \times 10^{+4}$  litres/gram-molecule-second. In Table 7 this value is compared with the velocities of other bimolecular reactions in solution and in the gaseous phase. Column 4 gives the fraction of the total number of

Table 7

Reaction	$E$ (calories per gram mol.)	$k_{37^\circ\text{C}}$ (litres per gram mol. second)	$e^{-E/RT}$	$\left(\frac{k}{e^{-E/RT}}\right)$
Inversion of sucrose by saccharase in aqueous solution	8,700	$4.2 \times 10^{+4}$	$7.0 \times 10^{-7}$	$0.6 \times 10^{11}$
Reaction between sodium ethoxide and ethyl iodide in ethylalcoholic solution	20,650	$3.5 \times 10^{-4}$	$2.3 \times 10^{-15}$	$1.5 \times 10^{11}$
Decomposition of hydrogen iodide in the gaseous phase	44,450	$4.2 \times 10^{-21}$	$3.5 \times 10^{-32}$	$1.2 \times 10^{11}$

molecules with a critical energy of  $E$  in two square terms. The enzyme reaction is seen to fall in line with the others. Its great speed is due primarily to the relatively large proportion (approximately one in a million) of the molecules which are in the active state at any instant. The parallelism between the figures in columns 3 and 4 is

explicable in terms of the general theory of activation, of which the collision theory is one variant. The approximate constancy of the quantities in the last column becomes intelligible in the light of the collision theory. It is well to recall that the results given in this table are based entirely upon experimental facts; although best understood in terms of the collision hypothesis, they possess an intrinsic value, independent of any theory.

## APPENDIX I

### *Notes on the Statistical Formulation of Velocity Constants*

STATISTICAL thermodynamics is the name given to the relatively new science which deals, from a mathematico-dynamical standpoint, with the properties of matter at equilibrium. It has proved possible, in certain instances, to extend its methods to systems which are departing from, or are striving towards, the equilibrium state. Such systems have, up to the present, been confined to simple molecules, undergoing unitary changes in the dilute gaseous state, and do not include solutions, in which complex molecules undergo chemical change by a concerted set of reactions. That is why the subject, important enough in itself, must here be dealt with as an Appendix.

We have first to deal with the partition function, starting from fundamental principles; then with the formulation of the laws of chemical equilibrium in the dilute gaseous state. There follows a description of how these laws may be extended to cover systems wherein equilibrium has not been achieved. Finally, some remarks are added concerning the possibility of extending to the kinetics of reactions in solution certain methods which have proved promising in the study of unitary chemical changes in the infinitely dilute gaseous state.

#### *The Partition Function*

The partition function, a dimensionless quantity, as its name implies, summarizes in convenient mathematical form the way in which the energy of a system of molecules is partitioned among the molecular inhabitants. Its value depends on the molecular weight, the temperature, the molecular volume, the internuclear distances, the molecular motions, and the intermolecular forces. The partition function provides the most convenient bridge yet devised for linking the microscopic properties of individual molecules (such as their discrete energy levels, moments of inertia, and dipole moments) with the macroscopic properties (such as molar heat, entropy, and polarization) of a system containing a large number of molecules. In any system of molecules at equilibrium, the number possessing an energy  $\epsilon$  each is proportional to the Boltzmann factor,  $e^{-\epsilon/kT}$ , where  $e$  is the base of the natural logarithms,  $\epsilon$  is the energy of one molecule,  $k$  is the Boltzmann constant ( $1.372 \times 10^{-16}$  erg/degree), and  $T$  is the absolute temperature. In such a system there is a certain number

(say  $N_1$ ) of molecules possessing energy  $\epsilon_1$  each; another number (say  $N_2$ ) possessing energy  $\epsilon_2$  each; and so on. The total number,  $N$ , of molecules in the system is

$$N = N_1 + N_2 + N_3 + \dots = \sum N_i, \quad (1)$$

and the total energy of the system is

$$E = N_1 \epsilon_1 + N_2 \epsilon_2 + N_3 \epsilon_3 + \dots = \sum N_i \epsilon_i. \quad (2)$$

The partition function, usually denoted by  $f$ , is simply the sum of all these Boltzmann factors, i.e.

$$f = e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + e^{-\epsilon_3/kT} + \dots. \quad (3)$$

As the molecular energy increases, the Boltzmann factor decreases. Energy among molecules is like money among men: the poor are numerous, the rich few. The series represented by equation (3) rapidly converges, and, although in principle we should always sum to infinity, in practice it is sometimes sufficient to count only the first ten terms or so. For generality, equation (3) is therefore summarized as follows:

$$f = \sum_{i=0}^{i=\infty} e^{-\epsilon_i/kT}, \quad (4)$$

where  $\epsilon_i$  is the energy possessed by a molecule in the  $i$ th state. The Boltzmann law is expressed mathematically as follows:

$$N_1 = K e^{-\epsilon_1/kT}, \quad (5)$$

where  $K$  is a constant for the system considered. Similarly, the numbers of molecules occupying groups in the higher energy levels are

$$N_2 = K e^{-\epsilon_2/kT},$$

$$N_3 = K e^{-\epsilon_3/kT},$$

$$\cdot \cdot \cdot \cdot \cdot$$

On adding, and using equations (1) and (3), we find that

$$N = K f. \quad (6)$$

Eliminating  $K$  from equations (5) and (6), we see that  $N_1/N = e^{-\epsilon_1/kT}/f$ , and, generally, that

$$\frac{N_i}{N} = \frac{e^{-\epsilon_i/kT}}{f}. \quad (7)$$

From this equation we note that the partition function,  $f$ , bears the same relation to the total number of molecules,  $N$ , as the Boltzmann factor bears to the number,  $N_i$ , of molecules in the specified energy level,  $\epsilon_i$ . The partition function is thus simply a generalized Boltzmann factor. The grand partition function,  $F$ , is related to  $f$  as follows:

$$F = f^N. \quad (8)$$

*The Relation of the Partition Function to Certain Thermodynamic Functions*

Let us differentiate equation (3) with respect to temperature at constant volume. We have

$$\left(\frac{df}{dT}\right)_V = \frac{\epsilon_1}{kT^2} e^{-\epsilon_1/kT} + \frac{\epsilon_2}{kT^2} e^{-\epsilon_2/kT} + \dots = \frac{1}{kT^2} \sum_0^\infty \epsilon_i e^{-\epsilon_i/kT}. \quad (9)$$

Multiplying throughout by  $kT^2$ , dividing throughout by  $f$ , and noting that  $dx/x$  equals  $d \ln x$ , we obtain

$$kT^2 \left(\frac{d \ln f}{dT}\right)_V = \frac{e^{-\epsilon_1/kT}}{f} \epsilon_1 + \frac{e^{-\epsilon_2/kT}}{f} \epsilon_2 + \dots = \frac{1}{f} \sum_0^\infty e^{-\epsilon_i/kT} \epsilon_i. \quad (10)$$

For the various ratios in this equation, let us substitute the number ratios to which, according to equation (7), they are equal. We then see that

$$NkT^2 \left(\frac{d \ln f}{dT}\right)_V = N_1 \epsilon_1 + N_2 \epsilon_2 + N_3 \epsilon_3 + \dots = \sum_0^\infty N_i \epsilon_i. \quad (11)$$

Clearly, the sum of the various products (number of molecules in a given energy group)  $\times$  (energy of each molecule in that group) represents the total energy,  $E$ , of the whole system of  $N$  molecules. Hence, by combining equations (2) and (11), we deduce that

$$E = NkT^2 \left(\frac{d \ln f}{dT}\right)_V, \quad (12)$$

which is the general relation between the total energy,  $E$ , of a system of  $N$  similar molecules at constant temperature,  $T$ , and the molecular partition function,  $f$ .

When a system is at equilibrium, the mathematical probability,  $W$ , of its existence, and its entropy,  $S$ , have maximum values. That there is a relation between  $W$  and  $S$  is obvious, but it was Boltzmann who first concluded that  $S$  is solely a function of  $W$  and that the relation must be a logarithmic one. By virtue of the third law of thermodynamics, established during this century, Boltzmann's relation may now be expressed in the simple form:

$$S = k \ln W. \quad (13)$$

The mathematical probability of a system is defined as the number of distinguishable ways in which that system can be realized.  $N$  molecules may be arranged in  $N!$  ways, but not all these arrangements are distinguishable. If  $N_1$  molecules have all the same energy,  $\epsilon_1$ ,

arrangements within this group will lead to indistinguishable configurations. Similarly, rearranging all the  $N_2$  molecules in the group having energy  $\epsilon_2$  per molecule leads to no new distinguishable arrangements. The total number,  $N!$ , of conceivable arrangements must thus be reduced by the product  $N_1! N_2! N_3! \dots$ , since each of these numbers represents the number of ways in which molecules in a given energy group can be arranged. We thus have

$$W = \frac{N!}{N_1! N_2! N_3! \dots} = N! \left( \prod^i N_i \right)^{-1}. \quad (14)$$

Combining equations (13) and (14), and making use of Stirling's approximation,  $\ln x! = x \ln x - x$ , (15)

which is valid when  $x$  is large, we may cast equation (13) into the following form:

$$\begin{aligned} \frac{S}{k} &= \ln W = N \ln N - N \\ &\quad - \left\{ \begin{aligned} &N_1 \ln N_1 - N_1 \\ &N_2 \ln N_2 - N_2 \\ &N_3 \ln N_3 - N_3 \\ &\vdots \quad \vdots \quad \vdots \end{aligned} \right\}. \end{aligned} \quad (16)$$

According to equation (1), however, the numbers in the last column cancel out, leaving

$$\frac{S}{k} = N \ln N - \sum N_i \ln N_i. \quad (17)$$

By writing equation (7) in logarithmic form, we see that

$$\ln N_i = \ln N - \frac{\epsilon_i}{kT} - \ln f, \quad (7)$$

and, consequently, that

$$N_i \ln N_i = N_i \ln N - \frac{N_i \epsilon_i}{kT} - N_i \ln f.$$

The sum of all such terms is

$$\begin{aligned} \sum N_i \ln N_i &= N_1 \ln N - \frac{N_1 \epsilon_1}{kT} - N_1 \ln f \\ &\quad + N_2 \ln N - \frac{N_2 \epsilon_2}{kT} - N_2 \ln f \\ &\quad + N_3 \ln N - \frac{N_3 \epsilon_3}{kT} - N_3 \ln f \\ &\quad + \dots \dots \dots \dots \\ &= N \ln N - \sum \frac{N_i \epsilon_i}{kT} - N \ln f. \end{aligned} \quad (18)$$

By means of equation (2), we therefore have

$$\frac{S}{k} = \frac{E}{kT} + N \ln f. \quad (19)$$

Substituting for  $E$  the expression already derived (equation (12)), we thus arrive at the general relation between the entropy,  $S$ , and the partition function,  $f$ :

$$S = Nk \left\{ \ln f + T \left( \frac{d \ln f}{dT} \right)_V \right\}. \quad (20)$$

Helmholtz defined the free energy, or maximum work term,  $A$ , as follows:

$$A = E - TS. \quad (21)$$

Inserting the general expressions derived above for  $E$  and  $S$ , we have

$$A = -NkT \ln f. \quad (22)$$

Equations (12), (20), and (22) may be regarded as key equations, from which the relationship between  $f$  and thermodynamic functions other than  $E$ ,  $S$ , and  $A$ , may readily be derived.

### *The Conditions of Chemical Equilibrium*

Let us suppose that the free energy,  $A$ , of a system containing  $N_1$  molecules of one kind,  $N_2$  molecules of another kind, and so on, can be expressed as a function of these numbers and of the constant volume,  $V$ , and temperature,  $T$ . The chemical potential of the first type of molecule is

$$\mu_1 = \left( \frac{dA}{dN_1} \right)_{V,T,N_2,N_3,\dots} \quad (23)$$

and of the second kind is

$$\mu_2 = \left( \frac{dA}{dN_2} \right)_{V,T,N_1,N_3,\dots}. \quad (24)$$

In general  $\mu_i = \left( \frac{dA}{dN_i} \right)_{V,T,N_j,N_k,\dots}$ .

In order that molecules of one kind shall be at equilibrium with those of another kind, the following thermodynamic law must hold

$$\sum \mu_i = \sum \mu_j. \quad (26)$$

Here the subscripts on one side of the equation refer to reactants and those on the other side to resultants. Equilibria in which we are especially interested are those in which molecules of types 1, 2, 3,... form a complex. The relevant law is then simply

$$\mu_1 + \mu_2 + \mu_3 + \dots = \mu_c. \quad (27)$$

### *Examples of Simple Partition Functions*

A glance at equation (3) shows that the partition function can always be evaluated numerically when the discrete energy levels of the molecules are known. These levels may be found either experimentally, by analysing the absorption and emission of radiation in the various spectral regions, or theoretically, by solving the Schrödinger equation for the appropriate molecular motions. The former method is the only one at present available in the study of complex molecules. The latter method is applicable to simple molecules, and to simple motions executed by complicated molecules.

(i) *Free linear motion.* For the linear motion of a point particle, of mass  $m$ , moving freely along a length  $l$ , the kinetic energy is

$$\epsilon = \frac{1}{2}mv^2 = \frac{1}{2m}(mv)^2 = \frac{1}{2m}\left(\frac{\hbar}{\lambda}\right)^2, \quad (28)$$

where  $\lambda$  is the de Broglie wavelength, one-half of which must be an integral fraction of  $l$ , i.e.  $\lambda = 2l/n$ . The discrete energy levels allowed by quantum laws are then

$$\epsilon = \frac{\hbar^2 n^2}{8ml^2} \quad (n = 1, 2, 3, \dots). \quad (29)$$

According to equation (3), the partition function is

$$f = \sum_{n=1}^{n=\infty} e^{-\hbar^2 n^2 / 8ml^2 kT}. \quad (30)$$

With sufficient accuracy for most purposes the summation yields the following result:

$$f = \frac{(2\pi mkT)^{\frac{1}{2}l}}{\hbar}. \quad (31)$$

When an atom, or a coherent group of atoms, is being torn from the remainder of a complex molecule, its relative motion when it is about to break away resembles linear translation in a force-free field. Equation (31) is therefore of interest in chemical kinetics.

(ii) *Free superficial motion.* The same considerations applied to the motion of a point particle free to move simultaneously along a length  $l_1$  in one direction and a length  $l_2$  in another direction at right angles to it, lead to the partition function

$$f = \frac{(2\pi mkT)^{\frac{1}{2}l_1}}{\hbar} \frac{(2\pi mkT)^{\frac{1}{2}l_2}}{\hbar}. \quad (32)$$

But  $l_1 l_2$ , which may be denoted by  $O$ , represents the area accessible to the molecule, so that

$$f = \frac{2\pi m k T O}{h^2}. \quad (33)$$

This equation is the general jumping-off ground afforded by statistical theory for the treatment of surface phenomena, such as interfacial tension and superficial adsorption.

(iii) *Free motion in a confined space.* Suppose the particle were capable of performing free superficial translation on a plane area,  $O$ , and simultaneously of executing free linear motion of extension  $l_3$ , in a direction at right angles to the plane. We should then find for the partition function the product

$$f = \frac{2\pi m k T O}{h^2} \frac{(2\pi m k T)^{\frac{1}{2}} l_3}{h}. \quad (34)$$

Now  $Ol_3$  is the volume,  $v$ , accessible to the molecule; hence

$$f = \frac{(2\pi m k T)^{\frac{1}{2}} v}{h^3}, \quad (35)$$

which is the partition function for a point particle, of mass  $m$ , free to move in (but confined to) a cell of volume  $v$  at temperature  $T$ .

(iv) *Free motion in a shared space.* Let us consider a number,  $N$ , of chemically identical molecules, each of which is capable of free translatory motion within a cell of average volume,  $V$ . By equation (8), the grand partition function is  $[(2\pi m k T)^{\frac{1}{2}} V/h^3]^N$ . Suppose the molecules, instead of being confined to the  $N$  different cells, were interchangeable, each interchange leading to a new molecular configuration which is indistinguishable from the original one. The grand partition function for the new system would be

$$[(2\pi m k T)^{\frac{1}{2}} V/h^3]^N/N!,$$

since  $N!$  is the number of arrangements of  $N$  particles. The system thus envisaged corresponds to that well-known and very helpful conception of the chemist known as the ideal gas, in which a total volume  $V$  is shared by  $N$  molecules, each occupying on an average a volume  $v (= V/N)$ . Making use of equations (8) and (15), we thus obtain, for the partition function of an ideal gas molecule of mass  $m$ , at temperature  $T$ :

$$f = \frac{(2\pi m k T)^{\frac{1}{2}} v e}{h^3}. \quad (36)$$

(v) *Harmonic motion.* According to the quantum theory, the energy of a linear oscillator executing simple harmonic vibration of frequency  $\nu$  is  $\epsilon = (s + \frac{1}{2})\hbar\nu$  ( $s = 0, 1, 2, \dots$ ). (37)

The partition function is therefore

$$f = \sum_0^{\infty} e^{-(s+\frac{1}{2})\hbar\nu/kT} = e^{-\hbar\nu/2kT}(1 + e^{-\hbar\nu/kT} + e^{-2\hbar\nu/kT} + \dots).$$

But since  $1+x+x^2+x^3+\dots = (1-x)^{-1}$ , it follows that

$$f = e^{-\hbar\nu/2kT}(1 - e^{-\hbar\nu/kT})^{-1}. \quad (38)$$

When the vibratory motion of a molecule about a mean position of equilibrium may be resolved into three vibratory motions, each of which is a simple harmonic one, the partition function becomes

$$f = e^{-\hbar(\hbar\nu_1 + \hbar\nu_2 + \hbar\nu_3)/kT}(1 - e^{-\hbar\nu_1/kT})^{-1}(1 - e^{-\hbar\nu_2/kT})^{-1}(1 - e^{-\hbar\nu_3/kT})^{-1} \dots \quad (39)$$

when the frequencies are different, and

$$f = e^{-3\hbar\nu/2kT}(1 - e^{-\hbar\nu/kT})^{-3} \quad (40)$$

when the frequencies are identical. Omitting details, this is the partition function which corresponds to Einstein's familiar treatment of the specific heat of monatomic solids, such as the diamond.

(vi) *Free rotation.* The energy levels allowed by the quantum theory for the free rotation of a rigid particle of moment of inertia  $I$  is

$$\epsilon = \frac{J(J+1)\hbar^2}{8\pi^2 I} \quad (J = 1, 2, 3, \dots). \quad (41)$$

This rotational energy, however, can be realized in  $(2J+1)$  ways, each corresponding to a separate solution of the Schrödinger equation. The partition function is accordingly

$$f = \sum_0^{\infty} (2J+1)e^{-J(J+1)\hbar^2/8\pi^2IkT}. \quad (42)$$

The summation is readily evaluated when  $\{(2J+1)\hbar^2\}/8\pi^2I \ll kT$ , which holds for massive molecules generally, but for light molecules only at high temperatures. The result is

$$f = \frac{8\pi^2IkT}{\hbar^2}. \quad (43)$$

If the rotator is symmetrical, this partition function must be divided by an integer,  $\sigma$ , which is equal to the number of indistinguishable permutations obtained by the rotation of the molecule. Hence

$$f = \frac{8\pi^2IkT}{\sigma\hbar^2}. \quad (44)$$

(vii) *Complex partition functions.*† If a molecule is capable of  $n$  degrees of freedom of rotation, the rotational partition function may be shown to be

$$= \frac{1}{\pi\sigma} \left\{ \frac{8\pi^3(I_A^a I_B^b \dots I_G^g)^{1/n} kT}{\hbar^2} \right\}^{1/n}, \quad (45)$$

where  $I_A, I_B, \dots, I_G$  are the moments of inertia of the molecule and its independently rotating parts;  $a, b, \dots, g$  are the rotational degrees of freedom associated with the corresponding moments of inertia; and

$$a+b+\dots+g = n, \quad (46)$$

and  $\sigma$  is the symmetry factor. Thus, when  $n = 3$ ,

$$f = \frac{\pi^4(8\pi^2kT)^{1/3}(I_A I_B I_C)^{1/3}}{\sigma\hbar^3}; \quad (47)$$

and when  $n = 2$  (in which case  $I_A$  equals  $I_B$ ),

$$f = \frac{8\pi^2IkT}{\sigma\hbar^2}. \quad (44)$$

The complex equation may be regarded as a generalization of these simpler cases, for which the partition functions are easily obtained. The value of the general expression will be instantly appreciated in any attempt to calculate the partition function of a molecule such as tertiary butane, where the rotation of the four methyl groups as well as the rotation of the whole molecule have to be considered.

When the various modes of motion make independently variable contributions to the total energy, the partition function,  $f$ , for a complex molecule, is the product of the separate partition functions,  $f_1, f_2, \dots$  for each mode of motion:

$$f = f_1 \times f_2 \times f_3 \times \dots \quad (48)$$

Generally, a molecule containing  $N$  atoms has in all  $3N$  degrees of freedom. Of these, 3 are devoted to the translation of the molecule as a whole, leaving a number  $3N - 3$  for the internal motions, rotational and vibrational. It is quite optional whether we regard the three degrees of rotation of the molecule as a whole as internal motions. If we do, the number of internal motions left is clearly  $3N - 6$ . Now let us consider that the motions are independently variable, that is, that we may, for example, excite one vibrational

† See R. H. Fowler, *Statistical Mechanics*, 2nd ed., Cambridge, (1936); K. F. Herzfeld, *Kinetische Theorie der Wärme*, Müller-Pouillet's *Handbuch der Physik*, Braunschweig, (1925); E. Schrödinger, *Statistical Thermodynamics*, Cambridge, (1946); E. A. Moelwyn-Hughes, *Physical Chemistry*, Cambridge, (1940).

degree of freedom without in any way altering the vibrational frequencies and the moments of inertia which characterize the remaining motions of which the molecule is capable. We then have for the total partition function in a force-free field

$$f = \frac{(2\pi mkT)^{1/2}}{\hbar^3} \frac{1}{\pi\sigma} \left\{ \frac{8\pi^3 (I_A^a I_B^b \dots I_C^g)^{1/2} kT}{\hbar^2} \right\}^{1/2} \prod_{i=1}^{3N-3-n} (1 - e^{-hv_i/kT})^{-1}. \quad (49)$$

When  $N = 3$ , and the vibrations are not degenerate, the expression becomes

$$f = \frac{(2\pi mkT)^{1/2}}{\hbar^3} \frac{1}{\pi\sigma} \frac{(8\pi^2 kT)^{1/2} (I_A I_B I_C)^{1/2}}{\hbar^3} \times \\ \times (1 - e^{-hv_1/kT})^{-1} (1 - e^{-hv_2/kT})^{-1} (1 - e^{-hv_3/kT})^{-1}; \quad (50)$$

when  $N = 2$ , we have

$$f = \frac{(2\pi mkT)^{1/2}}{\hbar^3} \frac{8\pi^2 I k T}{\sigma \hbar^2} (1 - e^{-hv/kT})^{-1}, \quad (51)$$

When  $N = 1$ , there can be no internal motions (since  $3N-3 = 0$ ), and we recover equation (36).

### *The Formulation of Simple Equilibria in the Gaseous State*

We shall now apply equation (26) to derive the equilibrium laws for some fairly simple chemical reactions in the ideally dilute gaseous phase. It will be convenient to introduce a new variable,  $q$ , defined as follows in terms of the concentration,  $n$ , the partition function,  $f$ , and the base of the natural logarithm,  $e$ :

$$q = nf/e. \quad (52)$$

Because the ideal gas laws are supposed to hold, it follows that the equilibrium constant for the general reaction



is

$$K = \frac{n_L^l}{n_B^b n_C^c} = \frac{q_L^l}{q_B^b q_C^c} e^{-E_0/kT}, \quad (53)$$

where  $E_0$  is the increase in internal energy for the reaction at the absolute zero. A few special cases may now be considered.

1. *Equilibria of type A  $\rightleftharpoons X$ .* Suppose that the molecule  $A$  is converted by acquisition of energy  $E_0$  into a molecule  $X$ , the process being either an isomerization or an activation, according as  $A$  loses or retains its original molecular structure. To express the equilibrium

constant, which in this case is a dimensionless quantity, we require only the ratio of the partition functions for the two species. In general, all the partition functions, with the exception of the translational function, are altered during the change. When only the vibrational degrees of freedom are excited, we may, as an approximation, consider all the other factors in the total partition functions of  $A$  and  $X$  to be identical, hence

$$K = \frac{n_X}{n_A} = \frac{q_X}{q_A} = \frac{\prod_{j=1}^i (1 - e^{-\hbar\nu_j(X)/kT})^{-1}}{\prod_{j=1}^i (1 - e^{-\hbar\nu_j(A)/kT})^{-1}} e^{-E_0/kT}. \quad (54)$$

Now the acquisition of vibrational energy generally loosens at least one bond. Let us denote the frequency of this weak bond in the molecule  $X$  by  $\nu_x$ , so that

$$K = \frac{(1 - e^{-\hbar\nu_x/kT})^{-1} \prod_{j=1}^{i-1} (1 - e^{-\hbar\nu_j(X)/kT})^{-1}}{\prod_{j=1}^i (1 - e^{-\hbar\nu_j(A)/kT})^{-1}} e^{-E_0/kT}. \quad (55)$$

Since, however, for small values of  $\hbar\nu_x/kT$ , we have the approximate relation

$$(1 - e^{-\hbar\nu_x/kT})^{-1} = \frac{kT}{\hbar\nu_x}, \quad (56)$$

the equilibrium constant becomes

$$K = \frac{kT}{\hbar\nu_x} \frac{\prod_{j=1}^{i-1} (1 - e^{-\hbar\nu_j(X)/kT})^{-1}}{\prod_{j=1}^i (1 - e^{-\hbar\nu_j(A)/kT})^{-1}} e^{-E_0/kT}. \quad (57)$$

A further simplification is possible if we are prepared to regard all the frequencies in the molecule  $X$  as identical with those of the original molecule  $A$ , except the one for the excited bond, which has the value  $\nu_x$  in  $X$  and  $\nu_a$  in  $A$ . Under these conditions, we have the very simple formula

$$K = \frac{n_X}{n_A} = \frac{kT}{\hbar\nu_x} (1 - e^{-\hbar\nu_a/kT}) e^{-E_0/kT}. \quad (58)$$

Finally, if the vibration frequency,  $\nu_a$ , of the bond which is excited is very high,

$$K = \frac{kT}{\hbar\nu_x} e^{-E_0/kT}. \quad (59)$$

The assumptions leading to these formulae have been carefully pointed out, and must not be overlooked.

2. *Equilibria of type A + B ⇌ AB.* The equilibrium established between free atoms of type A and B and the stable diatomic molecule AB is, according to equations (36) and (51), governed by the relation

$$K = \frac{n_{AB}}{n_A n_B} = \frac{q_{AB}}{q_A q_B} e^{-E_0/kT}$$

$$= \frac{\frac{(2\pi(m_A+m_B)kT)^{\frac{1}{2}}}{h^3} \frac{8\pi^2 I_{AB} kT}{h^2} (1 - e^{-hv_{AB}/kT})^{-1}}{\frac{(2\pi m_A kT)^{\frac{1}{2}}}{h^3} \frac{(2\pi m_B kT)^{\frac{1}{2}}}{h^3}} e^{-E_0/kT}, \quad (60)$$

provided A and B are dissimilar and provided the vibrations executed by the molecule are simple harmonic. Rearranging the terms, and noting that

$$I_{AB} = \frac{m_A m_B}{m_A + m_B} r_{AB}^2 = \mu_{AB} r_{AB}^2, \quad (61)$$

we have  $K = h r_{AB}^2 \sqrt{\left(\frac{8\pi}{kT \mu_{AB}}\right)} (1 - e^{-hv_{AB}/kT})^{-1} e^{-E_0/kT}.$  (62)

When  $h\nu \gg kT$ , the equation reduces to

$$K = h r_{AB}^2 \sqrt{\left(\frac{8\pi}{kT \mu_{AB}}\right)} e^{-E_0/kT}, \quad (63)$$

and when  $h\nu \ll kT$ , we have

$$K = \frac{r_{AB}^2}{v_{AB}} \sqrt{\left(\frac{8\pi kT}{\mu_{AB}}\right)} e^{-E_0/kT} \quad (64)$$

3. *Equilibria of the type A + BC ⇌ ABC.* Let us consider the equilibrium established between free atoms A and diatomic molecules BC on the one hand, and linear triatomic molecules ABC on the other hand, such as might hold for the chemical reaction between atoms of sulphur and molecules of carbon monoxide:



Making the usual assumption of harmonic vibrations and rigid rotations we obtain the equilibrium constant:

$$K = \frac{n_{ABC}}{n_A n_{BC}} = \frac{q_{ABC}}{q_A q_{BC}} e^{-E_0/kT}$$

$$= \frac{\frac{(2\pi(m_A+m_B+m_C)kT)^{\frac{1}{2}}}{h^3} \frac{8\pi^2 I_{ABC} kT}{h^2} \cdot \prod_{i=1}^4 (1 - e^{-hv_i/kT})^{-1}}{\frac{(2\pi m_A kT)^{\frac{1}{2}}}{h^3} \frac{(2\pi(m_B+m_C)kT)^{\frac{1}{2}}}{h^3} \frac{8\pi^2 I_{BC} kT}{h^2} (1 - e^{-hv_{BC}/kT})^{-1}} e^{-E_0/kT},$$

which, after cancelling and rearranging, becomes

$$K = \frac{h^3}{(2\pi kT)^{\frac{1}{2}}} \left( \frac{m_A + m_B + m_C}{m_A(m_B + m_C)} \right)^{\frac{3}{2}} \frac{I_{ABC}}{I_{BC}} \frac{\sigma_{BC}}{\sigma_{ABC}} \prod_{i=1}^4 \frac{(1 - e^{-h\nu_i/kT})^{-1}}{(1 - e^{-h\nu_{BC}/kT})^{-1}} e^{-E_0/kT}. \quad (65)$$

Of the three vibrations executed by the molecule  $ABC$ , let us suppose that one of them, say the transverse motion, has a low frequency,  $\nu_t$ , in which case we may write  $(1 - e^{-h\nu_t/kT})^{-1} = kT/h\nu_t$ . Of the other motions, the bending one (frequency =  $\nu_\phi$ ) is doubly degenerate, since the molecule can bend equally in two planes at right angles to each other, and the symmetrical motion (frequency =  $\nu_s$ ) is single. Hence

$$K = \frac{1}{\nu_t} \left( \frac{h}{2\pi} \right)^2 \left( \frac{2\pi}{kT} \right)^{\frac{1}{2}} \left( \frac{m_A + m_B + m_C}{m_A(m_B + m_C)} \right)^{\frac{3}{2}} \frac{I_{ABC}}{I_{BC}} \frac{\sigma_{BC}}{\sigma_{ABC}} \times \frac{(1 - e^{-h\nu_s/kT})^{-1} (1 - e^{-h\nu_\phi/kT})^{-2}}{(1 - e^{-h\nu_{BC}/kT})^{-1}} e^{-E_0/kT}. \quad (66)$$

$E_0$  is the difference between the internal energy of the product molecule ( $ABC$ ) and the energies of the atom  $A$  and reactant molecule ( $BC$ ), both molecules being in their lowest vibrational state at the absolute zero. The relation between the increase,  $(\Delta E)_T$ , in internal energy for the reaction, measured at any temperature, and defined by the van 't Hoff equation I (10), is found by differentiating the logarithm of  $K$ , as given here, and may be expressed thus:

$$\frac{(\Delta E)_T}{N_0} = E_0 - \frac{1}{2}kT - \frac{1}{2}h(\nu_s(1 - \coth \beta \nu_s) + 2\nu_\phi(1 - \coth \beta \nu_\phi) - \nu_{BC}(1 - \coth \beta \nu_{BC})), \quad (67)$$

where  $\beta = h/2kT$ .

The application of equation (66) to chemical kinetics is most conveniently made when it is rewritten in a slightly modified form, so as to contain the difference,  $E_s$ , between the energies of reactants and resultants when both are in the hypothetical state of zero energy. As may readily be seen from the diagram, the static value,  $E_s$ , is related to the lowest observable value,  $E_0$ , by the following general relation:

$$E_0 + \frac{1}{2}h \sum \nu_{\text{reactants}} = E_s + \frac{1}{2}h \sum \nu_{\text{resultants}}. \quad (68)$$

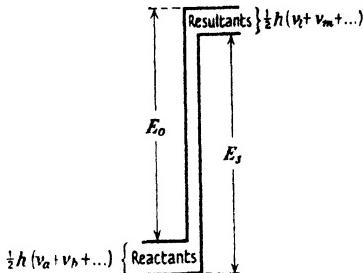
In the present example, the relation is

$$E_0 + \frac{1}{2}h\nu_{BC} = E_s + \frac{1}{2}h(\nu_s + 2\nu_\phi); \quad (69)$$

d d

hence equation (66) becomes

$$K = \frac{1}{\nu_t} \{f(T)f(m)f(I)f(\sigma)\} \frac{\left( \frac{e^{-\frac{1}{k}h\nu_s/kT}}{1 - e^{-h\nu_s/kT}} \right) \left( \frac{e^{-\frac{1}{k}h\nu_\phi/kT}}{1 - e^{-h\nu_\phi/kT}} \right)^2}{\left( \frac{e^{-\frac{1}{k}h\nu_{BC}/kT}}{1 - e^{-h\nu_{BC}/kT}} \right)} e^{-E_s/kT}. \quad (70)$$



Now  $\frac{e^{-\frac{1}{k}h\nu/kT}}{1 - e^{-h\nu/kT}} = \frac{1}{e^{+\frac{1}{k}h\nu/kT} - e^{-\frac{1}{k}h\nu/kT}} = \frac{1}{2 \sinh(\frac{1}{2}h\nu/kT)}.$

The equilibrium constant for the reaction  $A + BC \rightleftharpoons ABC$  thus becomes

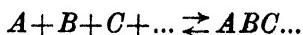
$$K = \frac{1}{4\nu_t} \left( \frac{h}{2\pi} \right)^2 \left( \frac{2\pi}{kT} \right)^{\frac{1}{2}} \left( \frac{m_A + m_B + m_C}{m_A(m_B + m_C)} \right)^{\frac{3}{2}} \frac{I_{ABC}}{I_{BC}} \frac{\sigma_{BC}}{\sigma_{ABC}} \frac{\sinh \beta \nu_{BC}}{\sinh \beta \nu_s \sinh^2 \beta \nu_\phi} e^{-E_s/kT}. \quad (71)$$

By direct differentiation with respect to temperature, or by comparing equations (67) and (69), we then have

$$\frac{(\Delta E)_T}{N_0} = E_s - \frac{1}{2}kT + \frac{1}{2}h(\nu_s \coth \beta \nu_s + 2\nu_\phi \coth \beta \nu_\phi - \nu_{BC} \coth \beta \nu_{BC}). \quad (72)$$

### *The Formulation of Simple Kinetic Expressions for Reactions in the Gaseous Phase*

The dominant conception of the Arrhenius theory is that equilibrium is maintained between passive and active molecules; and this has governed all recent developments.<sup>†</sup> We have seen that the equilibrium constant of the reaction



<sup>†</sup> Eyring and numerous collaborators, starting with *J. Chem. Physics*, **3**, 107, (1935); Polanyi and his school, starting with *Trans. Faraday Soc.*, **31**, 875, (1935); Horiuti, *Bull. Chem. Soc., Japan*, **13**, 210, (1938). See also Wigner and L. Farkas, *Trans. Faraday Soc.*, **32**, 708, (1936), and, for the slightly different version given here, Moelwyn-Hughes, *Physical Chemistry*, Cambridge, (1940).

may be expressed as follows

$$K = \frac{n_{ABC\dots}}{n_A n_B n_C \dots} = \frac{q_{ABC\dots}}{q_A q_B q_C \dots} e^{-E_0/kT}, \quad (73)$$

where  $q$  is defined by equation (52). The fundamental difference between an activated, but otherwise stable, molecule, and a reactive molecule is that one of the bonds in the latter has become so enfeebled by the activation that the molecule cannot survive a complete vibration in the weak bond. It seems natural to associate the rate of break-up of the reactive molecule or complex with the frequency of vibration, say  $\nu_x$ , in this weak bond. Now the rate of reaction, or the rate  $(+dn_p/dt)$  at which product molecules are formed, equals the rate at which the complex breaks down, and, omitting small and relatively unimportant factors, must equal the product of the concentration of complexes and the frequency,  $\nu_x$ , which governs the motion in the decomposition coordinate. We thus have

$$\begin{aligned} +\frac{dn_p}{dt} &= -\frac{dn_{ABC}}{dt} \\ &= n_{ABC} \nu_x \\ &= n_A n_B n_C \dots \times K \nu_x \\ &= n_A n_B n_C \dots \times \frac{q_{ABC\dots}}{q_A q_B q_C \dots} e^{-E_0/kT} \nu_x. \end{aligned}$$

But the specific velocity coefficient,  $k_n$ , for a reaction of the  $n$ th order is defined by the equation

$$+\frac{dn_p}{dt} = k_n n_A n_B n_C \dots;$$

hence  $k_n = \frac{q_{ABC\dots}}{q_A q_B q_C \dots} e^{-E_0/kT} \nu_x = K \nu_x, \quad (74)$

which is the desired general equation. A few of its simplest applications may now be given.

(1) For unimolecular reactions of the type  $A \rightleftharpoons X$ , we have seen that, subject to a number of stipulated conditions,

$$K = \frac{n_X}{n_A} = \frac{kT}{h\nu_x} e^{-E_0/kT}, \quad (59)$$

where  $\nu_x$  is the frequency in the active molecule  $X$ . It follows from equation (74) that the unimolecular velocity coefficient is

$$k_1 = \frac{kT}{h} e^{-E_0/kT}, \quad (75)$$

an expression first derived by Herzfeld.<sup>†</sup>

(2) For the bimolecular union of atoms  $A$  and  $B$ , we have seen that, when the frequency ( $\nu_{AB}$ ) in the molecule formed is low,

$$K = \frac{n_{AB}}{n_A n_B} = \frac{r_{AB}^2}{\nu_{AB}} \sqrt{\left(\frac{8\pi kT}{\mu}\right)} e^{-E_0/kT}; \quad (64)$$

hence

$$k_2 = r_{AB}^2 \sqrt{\left(\frac{8\pi kT}{\mu_{AB}}\right)} e^{-E_0/kT}, \quad \text{III (1)}$$

which is the equation of Trautz,<sup>‡</sup> of which frequent use has been made.

(3) In exactly the same way, from the equilibrium constant governing the union of an atom  $A$  with a molecule  $BC$  we simply multiply equation (71) by  $\nu_t$ , and find for the bimolecular velocity coefficient:

$$\begin{aligned} k_2 = & \frac{1}{4} \left( \frac{h}{2\pi} \right)^2 \left( \frac{2\pi}{kT} \right)^{\frac{1}{2}} \left( \frac{m_A + m_B + m_C}{m_A(m_B + m_C)} \right)^{\frac{3}{2}} \frac{I_{ABC}}{I_{AB}} \frac{\sigma_{BC}}{\sigma_{ABC}} \times \\ & \times \frac{\sinh \beta \nu_{BC}}{\sin \beta \nu_s \sinh^2 \beta \nu_\phi} e^{-E_m/kT}. \end{aligned} \quad (76)$$

This equation was first derived by Pelzer and Wigner.<sup>§</sup>

The factor  $P$  in equation III (4) for reactions of this type may be shown to be

$$\begin{aligned} P = & \left\{ \frac{h}{4\pi(r_A + r_B)} \right\}^2 \left( \frac{m_A + m_B + m_C}{m_A(m_B + m_C)} \right)^{\frac{3}{2}} \frac{I_{ABC}}{I_{BC}} \frac{\sigma_{BC}}{\sigma_{ABC}} \frac{\sinh \beta \nu_{BC}}{\prod_i \sinh \beta \nu_i^*} \times \\ & \times \exp - \left\{ \frac{1}{2} + \beta (\nu_{BC} \coth \beta \nu_{BC} - \prod_i \nu_i^* \coth \beta \nu_i^*) \right\}, \end{aligned} \quad (77)$$

where  $(r_A + r_B)$  is the critical distance between atom and molecule which one would use in equation III (1). In the many triatomic reactions involving hydrogen, deuterium, and bromine, the vibration frequencies have been calculated, and from them the values of  $P$  determined. They vary from 1.0 to 0.6 and are in all cases in satisfactory agreement with experiment.

Less simple relations are naturally found when we apply the same method to the kinetics of reactions involving more than three atoms.

<sup>†</sup> *Ann. Physik*, **59**, 635, (1919).

<sup>‡</sup> *Z. anorg. Chem.*, **96**, 1, (1916).

<sup>§</sup> *Z. physikal. Chem.*, **B**, **15**, 445, (1932); cf. L. Farkas and Wigner, *Trans. Faraday Soc.*, **32**, 708, (1936).

*The Extension of Statistical Principles to the Kinetics of Reactions in Solution*

It is a far cry from the three-atom system in an infinitely dilute gaseous medium to a sugar in water, and no rigorous treatment is at present to be contemplated.

The object of the following brief discussion is less to seek illumination from statistical theory than to indicate the direction in which we consider that theory should advance while retaining contact with facts.

For a solute molecule composed of  $N$  atoms in a solution so dilute that the mutual interaction of solute molecules may be neglected, we may propose the use of the partition function

$$f = \frac{g(2\pi mkT)^{\frac{1}{2}} v_f}{h^3} \frac{1}{\sigma} \left( \frac{8\pi^3 (I_A I_B \dots I_G)^{1/n} kT}{h^2} \right)^{\frac{1}{2}n} \prod_{i=1}^{3N-3-n} (1 - e^{-\hbar\nu_i/kT})^{-1} e^{-\phi/kT}, \quad (78)$$

where  $g$  is the degeneracy of the electronic level, and  $m$  is the mass of the solute molecule. The term  $v_f$  is the average free volume available to the solute molecule, and may be determined by extending to two-component systems the methods developed for pure liquids.†  $\sigma$  is a symmetry factor, and  $n$  the number of degrees of freedom of rotation of the solute molecule and its parts, to which the moments of inertia,  $I_A, I_B, \dots, I_G$  refer.  $\nu_i$  is the frequency of the  $i$ th of the internal vibrations, all of which are assumed to be simple harmonic. Finally,  $\phi$  is the average energy of interaction of the solute molecules with the solvent molecules which enclose it. Special forms of  $\phi$  have been considered by us in numerous papers. A similar expression, adjusted to a common reference level for the energy, obtains for the active molecule. Denoting the variables pertaining to the active molecule of solute by an asterisk, we then obtain for the ratio of the concentration,  $n^*$ , of active molecules to the concentration,  $n$ , of normal molecules, the equilibrium expression

$$\frac{n^*}{n} = \frac{v_f^* \left( \frac{I_A^* I_B^* \dots I_G^*}{I_A I_B \dots I_G} \right)^{\frac{1}{2}}}{v_f} \frac{\prod_{j=1}^{3N-3-n} (1 - e^{-\hbar\nu_j/kT})^{-1}}{\prod_{i=1}^{3N-3-n} (1 - e^{-\hbar\nu_i/kT})^{-1}} e^{-(\phi^* - \phi)/kT} e^{-\epsilon/kT}. \quad (79)$$

The terms  $v_f$  and  $v_f^*$  are molecular free volumes, and the expression

† See, for example, Lennard-Jones and Devonshire, *Proc. Roy. Soc., A*, **163**, 53, (1937).

holds for equilibrium established at constant total volume. The multiplicities of the electronic states have been assumed equal, and the number of modes of vibration not to change during activation.  $\epsilon + (\phi^* - \phi)$  is the energy of activation in a solution supercooled to the absolute zero of temperature.

The experimental magnitudes for the frequency terms,  $\nu_i$ , with reference to the normal solute molecule—as distinct from the gaseous molecule—are forthcoming from a study of the Raman spectra of solutions; and it is not difficult to compute reasonable values for the moments of inertia. Unfortunately, however, data for activated solute molecules are mostly lacking, and the advances in the kinetics of reactions in solution await comparable advances in the statics of solutions. Not before the latter have been made can one hope to derive from equation (79) the expression holding for equilibria at constant pressure and to take the further trivial step of thermodynamic annotation.

In the meanwhile, general statistical expressions have to be abbreviated by the cancellation or suppression of terms so as to make comparison with experiment possible. Before doing so, we recall that, in accordance with the general hypothesis of activation, the fate of most of the active molecules is reversion to type. Only a small number of the active molecules, insufficient to destroy the equilibrium ratio, suffer chemical change. The frequency with which such transformation of an active molecule occurs in the gas phase has been assumed by Herzfeld and others to be that of slowest internal motion of which the active molecule is capable. In the case of an active solute molecule, however, it may happen that the rate of destruction is governed by one of the frequencies of vibration of the molecule in its cage. This is thought to be especially relevant to reactive solutes in polar solvents, for which, as we have shown, one has to consider the activation of a whole cluster of molecules. If the forces exerted between solute molecules and solvent molecules are spherically symmetrical, we have the following approximate expression for the frequency of the intracellular vibration:

$$\nu = \frac{1}{2\pi} \left[ \frac{2cBm}{3!\mu r^{m+2}} \left\{ (n-1) \left( \frac{r_0}{r} \right)^{n-m} - (m-1) \right\} \right]^{\frac{1}{2}}. \quad (80)$$

Here  $c$  is the number of solvent molecules,  $\mu$  the reduced mass of the cluster (virtually equal to the mass of the solute),  $r$  the average

solute-solvent separation, and  $B$ ,  $m$ , and  $n$  are constants of the equation

$$\phi(r) = c\{Ar^{-n} - Br^{-m}\}. \quad (81)$$

A more exact form is available.<sup>†</sup> In the present equation, of course,  $B$  is the attractive energy constant for an isolated pair of unlike molecules. The product of the right-hand expressions in equations (79) and (80) gives us the unimolecular constant.

It is to be noted that the dependence of  $\nu$  on  $r$  is of the form necessary to explain the abrupt changes in reaction velocity in solution observed by Sutherland and Maas<sup>‡</sup> in the neighbourhood of the critical temperature.

The assumptions which must be made in order to compare these relations with experimental results in general are the following: (1) The difference between the observed velocity coefficient and that which would hold at constant volume must not be so great as to reverse the sign of  $C$  (equation I(6)). (2) The product of the intracellular vibration frequency and the first and fourth terms of equation (79) must be independent of temperature. The pre-exponential terms in the equilibrium expression thus reduces to a ratio of the products of the vibrational partition functions of the active and normal molecules. (3) In the normal molecule, let a number,  $p$ , of the vibrational motions be quantal, and a number,  $q$ , classical. The corresponding numbers for the active molecule may be denoted by the letters  $r$  and  $s$ . Then the unimolecular constant is

$$k_1 = \nu \times \frac{\prod_p^r (1 - e^{-hv_p/kT})^{-1} \prod_q^s (kT/hv_q)}{\prod_p^r (1 - e^{-hv_p/kT})^{-1} \prod_q^s (kT/hv_q)} e^{-\epsilon/kT}, \quad (82)$$

and consequently, if  $\epsilon_m$  stands for the difference in internal energy of the active and normal molecules considered statically at the absolute zero of temperature, we have

$$E_A/N_0 = \epsilon_m - (q-s)kT - \frac{1}{2} \sum_p^r h\nu_p \coth(h\nu_p/kT) + \frac{1}{2} \sum_q^s h\nu_q \coth(h\nu_q/kT). \quad (83)$$

This expression conforms with equation I(5) provided  $q > s$ . The conclusion is that it is impossible to loosen a reactive bond in the solute molecule without tightening the other bonds. In polar solvents,

<sup>†</sup> Lennard-Jones and Devonshire, *loc. cit.*, and Corner, *Trans. Faraday Soc.*, **35**, 711, (1939).

<sup>‡</sup> *Loc. cit.*

where long-range electrostatic forces have a co-ordinating influence on the mechanism of activation, it is not likely that the rate of activation is in any real sense a problem. The structural difference between normal and active molecules, and the rate at which the latter break up, seem to be more relevant.

As indicated in Chapter II, we now consider the experimental evidence sufficiently strong to warrant the generalization that unimolecular reactions in aqueous solution conform more closely to the following equation (cf. equation I(5))

$$\log_{10} k = c - b \log_{10} T - a/T, \quad (84)$$

than to the equation of Arrhenius. According to classical and quantal theories, the integer  $b$  is the number of feeble oscillations which take part in the activation. For example, the unimolecular constant,  $k_\alpha$ , governing the conversion of  $\alpha$ -glucose into  $\beta$ -glucose, may be expressed as follows (Table II (20)):

$$\log_{10} k_\alpha = 37.814 - 10 \log_{10} T - 5039.34/T. \quad (85)$$

Thus ten oscillations are involved, though the number is uncertain between 7 and 13. In the hydrolysis of methyl bromide, the number is so much higher ( $34 \pm 4$ ) that we may rule out a hydrolytic mechanism for mutarotation, which may be legitimately considered as a localized activation confined to the potentially aldehydic group and possibly one water molecule. This relative simplicity in the mechanism, coupled with the similarity of the outer sugar structure to water, suggests that our observations at constant pressure are not very different from those which would be obtained at constant volume. We shall therefore compare our results directly with equation (82). The effective mean frequency, defined by the relation

$$\bar{\nu} = \left( \nu \times \frac{\nu_1 \nu_2 \dots \nu_q}{\nu'_1 \nu'_2 \dots \nu'_s} \right)^{(q-s+1)^{-1}}, \quad (86)$$

is then found by experiment to be  $6.61 \times 10^{12}$  sec. $^{-1}$ , which lies near to the frequency  $kT/h$  ( $6.24 \times 10^{12}$  at  $T = 298.2^\circ$  K.). The corresponding mean wave number is  $220$  cm. $^{-1}$ . These results support the supposition of activation among feeble oscillators, some of which would appear to be of the hindered rotational type.

The exact comparison of theory and experiment requires information on the complicated question of the dependence of many of these oscillatory frequencies on temperature. Until such information

appears, we may regard the present theory as sufficiently clear in outline though blurred in detail.

In the accompanying table we give the results of calculations for certain reactions studied in this way. Columns 2 and 3 contain the experimental values of the energy of activation and effective mean frequency. In the last column is found the number of quanta,  $\hbar\nu$ , which will fully account for  $E_0$ . We infer that the activation energy in mutarotation is not drawn solely from oscillatory motions or that each oscillator contributes many quanta. In the other cases, the figures in columns 4 and 5 tally.  $q-s$  is about 21 for trinitrobenzoic acid and about 9 for trichloracetic acid; one is naturally inclined to attribute the difference of 12 to the three nitro groups, which may claim 4 each. When a molecule of trinitrobenzoic acid decomposes, therefore, the whole molecule contributes to the localized ejection of the three atoms.

Reactant in aqueous solution	$E_0$ cal./gm. mol.	$\bar{\nu} \times 10^{-13}$ sec. <sup>-1</sup>	$q-s$ obs.	$E_0/\hbar\nu$
$\alpha$ -Glucose	23,055	0.66	$10 \pm 3$	36.7
Tribromacetate ion	39,610	5.25	$10 \pm 5$	8.0
Trichloracetate ion	42,910	5.70	$10 \pm 5$	7.8
Methyl bromide	46,820	1.66	$34 \pm 4$	29.7
2:4:6-Trinitrobenzoate ion	52,300	2.95	$23 \pm 5$	18.7

## APPENDIX II

### *A List of Titles of Publications by the Author relating to the Kinetics of Chemical Reactions*

1. The Kinetics of the Hydrolysis of Certain Glykosides. Part I: Salicin, Arbutin, and Phloridzin, *Trans. Faraday Soc.*, **24**, 309, (1928).
2. The Kinetics of the Hydrolysis of Certain Glykosides. Part II: Trehalose,  $\alpha$ -Methylglucoside, and  $\alpha$ -Methyltetramethylglucoside, *ibid.*, **25**, 81, (1929).
3. The Kinetics of the Hydrolysis of Certain Glycosides. Part III:  $\beta$ -Methylglucoside, Cellobiose, Melibiose, and Turanose, *ibid.*, **25**, 503, (1929).
4. The Reactivity of Glucose in the Presence of Hydrochloric Acid. Part I: *ibid.*, **24**, 321, (1928).
5. The Reactivity of Glucose in the Presence of Hydrochloric Acid. Part II: *ibid.*, **25**, 435, (1929).
6. The Enzymic Hydrolysis of Phloridzin, *J. General Physiol.*, **13**, 807, (1930).
7. The Variation with Temperature of the Relative Rates of Hydrolysis of Glykosides, *ibid.*, **13**, 317, (1930).
8. The Kinetics of Enzyme Reactions: Schütz's Law (with J. Pace and W. C. McC. Lewis), *ibid.*, **13**, 323, (1930).
9. The Kinetics of Reactions in Solution. Part I: A Comparison of the Decomposition of Chlorine Monoxide in the Gaseous State and in Carbon Tetrachloride Solution (with C. N. Hinshelwood), *Proc. Roy. Soc., A*, **131**, 177, (1931).
10. The Kinetics of Reactions in Solution. Part II: The Decomposition of Trinitrobenzoic Acid in Various Solvents (with C. N. Hinshelwood), *ibid., A*, **131**, 186, (1931).
11. The Kinetics of the Decomposition, in Carbon Tetrachloride Solution, of Ozone and of Ozone-Chlorine Mixtures (with E. J. Bowen and C. N. Hinshelwood), *ibid., A*, **134**, 211, (1931).
12. The Kinetics of Reactions Involving Collisions Between Solute and Solvent Molecules, *Trans. Chem. Soc.*, 95, (1932).
13. The Kinetics of Two Bimolecular Reactions in Solution and in the Vapour Phase (with C. N. Hinshelwood), *ibid.*, 230, (1932).
14. The Kinetics of the Esterification of Acetic Anhydride in Ethyl-alcoholic Solution (with A. C. Rolfe), *ibid.*, 241, (1932).
15. The Lower Explosion Limit in the Reaction between Hydrogen and Oxygen (with C. N. Hinshelwood), *Proc. Roy. Soc., A*, **138**, 311, (1932).
16. The Kinetics of Certain Bimolecular Reactions in Solution, *Chem. Rev.*, **10**, 241, (1932).
17. The Kinetics of Chemical Change in Solution, *Phil. Mag.*, **14**, 112, (1932).

18. The Combination of Hydrogen and Oxygen in a Silver Vessel (with C. N. Hinshelwood and A. C. Rolfe), *Proc. Roy. Soc., A*, **139**, 521, (1933).
19. The Kinetics of the Oxidation of Picric Acid by Potassium Permanganate in Aqueous Solution (with F. F. Musgrave), *Trans. Faraday Soc.*, **29**, 1162, (1933).
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